Determination of the collisional energy transfer distribution responsible for the collision-induced dissociation of NO₂ with Ar

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Abstract

Collisional energy transfer is an essential aspect of chemical reactivity and maintenance of thermal equilibrium. Here we report the shape (energy-dependence) of the collisional energy transfer probability function for collisions of vibrationally excited NO₂ entrained in a molecular beam and photoexcited to within 40 cm⁻¹ of its dissociation threshold. The internally excited molecules undergo collisions with Ar atoms in a crossed beam apparatus. Dissociative collisions rapidly produce the NO(*J*) fragment, which is observed by velocity-mapped ion imaging and REMPI techniques. The measured collisional energy transfer function is obtained via energy conservation and is compared with the results of classical trajectory calculations. Good agreement between the theory and experiment is found for collisions that transfer small amounts of energy, but the theory predicts a higher likelihood of energetic collisions than is observed experimentally. We explore possible explanations for this discrepancy in the dynamics of the collision excitation process.

1. Introduction

Energy transfer to and from rotationally and vibrationally excited states underlies the processes of collisional stabilization, maintenance of thermal equilibrium, and pyrolysis important to chemically reactive systems such as flames. On a single chemical reaction level, the rates of many elementary reactions are pressure dependent, including unimolecular reactions that are rate-limited by energy transfer at low pressures and reactions that show falloff from their

high-pressure limit rate coefficients at moderate pressures. Due to the central importance of energy transfer in chemical reactivity, there is a long history of studies of collisional energy transfer of highly excited molecules. Almost 20 years ago, Flynn, Parmenter, and Wodtke reviewed the vast vibrational energy transfer literature and provided 465 references¹ including earlier reviews;^{2,3,4} numerous relevant papers have appeared since then.

Investigations involving both activating and deactivating collisions have been performed, but, in general, the study of collisional deactivation of highly vibrationally excited species has been more prevalent. Experimental information about collisional energy transfer can be obtained indirectly from low-pressure-limit unimolecular decomposition and isomerization kinetics, and such studies have been carried out for several small unimolecular systems in different atomic and molecular baths.⁵⁻⁸ More direct experimental studies of collisional energy transfer have also appeared. These have focused on characterizing the energy transfer function $P(E,E')$, which describes the probability that a collision changes the internal energy of the unimolecular species from some internal state E' to some other state E . In some studies, low-order moments of $P(E,E')$ have been obtained by following the time-dependent energy content either of the initially excited molecule or the (bath gas) collision partner, including the time-dependent IR emission studies of Barker^{9,10} and Dai^{11,12} and the time-resolved UV absorption spectroscopy experiments of Troe and co-workers.^{13,14} The work of Lenzer and Luther, through their kinetically controlled selective ionization studies, improved this overall approach by giving information about not only the average energy transferred but the shape of the $P(E,E')$ distribution^{15,16} and reconciled historical discrepancies¹⁷ between the earlier studies. Their work demonstrated that there is an energy dependence to both the first and second moment of the energy transfer distribution (the average energy transferred and the width of the energy transfer distribution). Their work also suggested the presence of “supercollisions,” low-probability events involving a very large degree of ro-vibrational/translational energy transfer, first predicted by Miller and Brown.¹⁸ It is accepted that most $P(E,E')$ curves from vibrationally hot polyatomic molecules are better described by a double exponential (or a stretched exponential) than a single exponential. The strong collisions that represent approximately 10% or less of the collisions that make up the long “supercollision” tail represent up to 25% of the energy transfer in some systems.

Supercollisions were first detected experimentally by Flynn and co-workers through high-resolution, diode laser transient absorption spectroscopy on collisionally excited

(rotationally and translationally) CO₂ as a collision partner of a very vibrationally hot perfluorobenzene molecule.¹⁹ These experiments are sensitive to the strong collisions that transfer large amounts of energy to the rotational and translational degrees of freedom of the CO₂ collision partner. As the experiment is performed in a bulb gas arrangement the CO₂ has an initial thermal distribution and therefore small amounts of energy transfer are not observed. These studies have been expanded by the Mullin^{20,21} and Sevy²² groups to many systems with either water or CO₂ as a collider gas. These experiments provide information on the energy transfer of collisions transferring approximately 1500 cm⁻¹ or larger. Great strides in understanding these energetic collisions for large benzene like molecules have been made with the development of the “GRETCHEN” model^{23,24} which has been able to demonstrate a strong correlation between the energy transfer for collisions transferring at least $E > 3000 \text{ cm}^{-1}$ with the density of states of the molecule in accord with Fermi’s Golden Rule.²⁵ From trajectory calculations on these systems, there remains uncertainty about the exact nature of the collisions with some calculations indicating that certain modes promote energetic collisions,²⁶ sometimes involving chattering collisions and complex formation,²⁷ some suggesting special collisions where a H atom was pinched between the backbone of the molecule and the collider molecule²⁸ were important, and others suggesting that rotational energy transfer of large torque were responsible for the high energy wing of the distribution.^{29,30}

Cold supersonic expansions for production of molecular beams provides a way to achieve greater state selectivity in the degree of internal excitation, as was shown by the experiments of Parmenter and co-workers that investigated vibrational energy transfer of excited electronic states^{31,32}. By employing two crossed-molecular beams for the collision experiments the advantage of initial state selectivity is coupled with well-defined large collision energies. Due to the selective excitation to a single ro-vibrational state in the excited electronic state, these crossed-beam experiments have the advantage of being able to observe both vibrational deactivating and activating collisions. These studies showed that even in very large molecules like p-difluorobenzene with large amounts of vibrational excitation transfers involving single quantum changes in the lowest frequency mode, $\nu'(30) = 120 \text{ cm}^{-1}$, are the dominant single channels for all levels. That is, the identity of the quantum states remains important to the energy transfer.

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4 The first crossed-beam studies of vibrationally excited molecules that focused upon
5 collisions of very vibrationally hot ground state molecules were those of Fisk and co workers in
6 the 1970's^{33,34,35} who studied energy transfer from hot KBr. More recently two groups have used
7 crossed molecular beam techniques to study vibrationally hot ground state molecules. In an
8 experimental arrangement very similar to the one we use here, Reisler and co-authors have also
9 investigated collisional excitation of highly-excited NO₂.^{36,37,38} These will be described in some
10 detail below as they are to be compared with the results we obtain here. Ni and co-workers^{39,40}
11 also used collisions in crossed supersonic atomic and molecular beams to measure the single
12 collision energy transfer between azulene and rare gas atoms. By ionizing the hot azulene that
13 has had a collision and measuring its velocity distribution utilizing velocity mapped sliced
14 imaging they were able to make a measurement of the shape of the energy transfer function,
15 $P(E,E')$. Subsequent trajectory calculations of this distribution were disappointingly unable to
16 match the experiment as the calculations predicted only a third of the energy transfer as the
17 experiments measured.⁴¹

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19 The NO₂ molecule provides an important benchmark system due to the plethora of
20 investigations into the collisional and photodissociation dynamics of the molecule. NO₂ is a
21 molecular system with a facile means for excitation and the NO products are easily detected by
22 resonant ionization of near UV light (~226 nm). While it is easy to produce a molecule with a
23 low degree of vibrational excitation one cannot generally produce a molecule vibrationally
24 excited to within a few wavenumbers below its dissociation limit. However, NO₂ can be excited
25 to a highly vibrationally excited state directly through one photon excitation to an excited
26 electronic state followed by internal conversion of this electronically excited state to the ground
27 state. The details of collisional energy transfer to NO₂* have previously been studied both in
28 crossed-beam and bath-gas experiments, such as the crossed-beam experiments Reisler and
29 coworkers mentioned above,³⁶ as well as a series of bath-gas experiments performed by Dai and
30 coworkers,^{11,12,42} and a state-to-state study by Abel et al.⁴³ that examined NO₂+NO₂ collisional
31 energy transfer. Like the present experiments reported here, the experiments of Reisler and co-
32 workers utilized collision induced dissociation followed by detection of the dissociation product,
33 NO(*J*), to monitor the energy transfer.³⁶ They were able to observe and quantify the shape of the
34 high energy tail of the energy transfer function associated with energy transfer greater than ~300
35 cm⁻¹. Our current study, utilizing a different detection scheme, is complementary to Reisler's

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4 study as it quantifies the lower energy region of the energy transfer function, *i.e.* energies lower
5 than $\sim 300\text{ cm}^{-1}$, and is sensitive to the shape of the distribution as well. There is a small region
6 of overlap between the two studies.
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10 Collisional energy transfer in highly vibrationally excited molecules has been studied
11 extensively using classical trajectory calculations. These calculations can yield detailed
12 information on the collisional energy transfer processes,^{18,44-54} but their accuracy can be limited
13 by the quality of the potential energy surfaces. Examples of recent studies include the collisional
14 energy transfer calculations of Barker et al., that examined the degree of excitation and de-
15 excitation of polyatomics in collisions with Ar,⁵⁵ the collisional stabilization calculations of
16 Babikov and co-workers,⁵⁶ and the allyl + Ar trajectory studies of Conte et al.^{57,58} The accuracy
17 of trajectory-based collisional energy transfer calculations can be inferred by comparing
18 predicted low-pressure-limit and pressure-dependent rate coefficients—which are sensitive to
19 collisional energy transfer—with available experimental results.⁵⁹⁻⁶² Such comparisons are
20 indirect, however. Differences in the theoretical and measured kinetics may arise due to other
21 aspects of the calculation. Here, we compare experimental and computed results for the detailed
22 energy transfer function, $P(E,E')$, which is much more direct test of the trajectory methods than
23 comparisons of highly averaged kinetics. As noted above, a similar comparison of $P(E,E')$ for
24 azulene + Ar showed qualitative, but not quantitative, agreement between the theoretical and
25 experimental results.^{39,40-41} The magnitude of this discrepancy is perhaps surprising in light of the
26 very accurate low-pressure kinetics predictions obtained using models that depend sensitively on
27 trajectory-based collisional energy transfer.⁶²
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43 Here we consider the shape (*i.e.*, the E -dependence) of the collisional energy transfer
44 function $P(E,E')$. This function is often approximated by an energy-gap or exponential-gap law,
45 where $P(E,E') = A \exp(-\Delta E/\alpha)$, $\Delta E = E - E'$, and α is related to the collision efficiency.
46 Trajectory calculations nearly universally show a more complicated shape for this function, one
47 that can be better modeled by a multiexponential decay function.¹⁸ With this in mind, we utilize a
48 novel experimental strategy for measuring the shape of the energy transfer distribution, $P(E,E')$,
49 of highly vibrationally excited NO₂ molecules in a collision with Ar atoms. The measured shape
50 of the energy transfer function is compared with the results of classical trajectory calculations.
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2. Methods

2.1. Experimental

The crossed-beam velocity-mapped ion imaging (VMII) apparatus utilized for the current experiment has been described previously.⁶³ As shown in the spatial schematic in panel (a) of Fig. 1, a pulsed nozzle jet expansion of pure Ar is crossed at 90 degrees with an expansion of approximately 15% NO₂ entrained in Ar, with 5% O₂ added to reduce the amount of NO in the beam, to investigate single-collision dynamics of NO₂ with Ar. The NO₂ molecules are photoexcited before the collisions by a pulsed dye laser with a λ_{pump} of 398.5 nm. The scattering products are probed with a second pulsed dye laser with a λ_{probe} (~226 nm) on the A–X transition of the NO(*J*) fragmentation products of the Ar collision with the excited NO₂. The NO₂ is photoexcited before the crossing region of the atomic and molecular beams, as shown in Fig 1. panel (a). Introducing a spatial separation between the photoexcitation and scattering center prevents the observation of photodissociation products of collisionally-excited ground-state NO₂ molecules that would be excited by the λ_{pump} .

The preparation of our highly vibrationally excited NO₂ molecules follows the scheme utilized by previous studies.^{11,36} Laser excitation of jet expansion-cooled NO₂ to the NO₂(A/B) state results in internal conversion to the overlapping NO₂(X) ground electronic state. As shown in the schematic in panel (b) of Fig. 1 the laser excitation of the NO₂ to a highly vibrational excited state (NO₂^{*}) with a λ_{pump} of 398.6 nm (25088 cm⁻¹) is 40 cm⁻¹ below the dissociation threshold, D_e . The dissociation threshold for NO₂(X) is 25128 cm⁻¹.^{64,65}

At the beam velocities employed, a collision of NO₂^{*} with Ar has sufficient energy to promote the NO₂^{*} to a ro-vibrationally excited state, NO₂^{**}, above the dissociation threshold. The barrierless dissociation of NO₂(X) produces fragments in their electronic ground state: NO(²Π) molecules and O(³P) atoms. The collisionally produced NO(*J*) fragments are detected by REMPI ionization. This scheme is illustrated by the REMPI spectrum and schematic in panel (b) of Fig. 1. By tuning the wavelength λ_{probe} around 226nm, specific rotational states of the NO fragment distributions are ionized. The ionization is performed in the ion lens of the VMII apparatus in order to measure the velocity distribution of the rotationally state selectively ionized NO fragments. The resultant velocity distribution of the NO fragments is the convolution of the original Ar+NO₂^{*} scattering dynamics and the subsequent NO₂^{**} → NO(*J*) + O dissociation dynamics, as discussed in detail below.

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4 The Newton diagram schematic of panel (c) in Fig. 1 illustrates the relative components
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6 in velocity space. The nozzle jet expansion of NO₂ entrained in Ar results in a velocity
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8 distribution with a mean of 560 m/s and a FWHM of 100 m/s. The same velocity distribution
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10 characteristics are measured for the neat Ar beam by seeding a small amount of NO into the Ar
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12 beam and using the VMII apparatus to determine the velocity and velocity spread. At a collision
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14 angle of 90 degrees, these velocities result in a collision energy distribution with a mean of 560
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16 cm⁻¹ and a FWHM of 140 cm⁻¹. The elastic scattering of NO₂* shown by the large gray circle
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18 demonstrates the conservation of all kinetic energy in either NO₂* or Ar velocities. Only the
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20 collisions which impart internal energy to the NO₂* molecule by removal of some of the total
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22 kinetic energy to make NO₂** are capable of producing fragment NO(*J*) molecules that are
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24 imaged. A single velocity map ion image of a given NO(*J*) state is acquired by averaging over
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26 many laser pulses. Depending upon signal intensity, averages were accumulated over 5 to 10
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28 hours utilizing 30 Hz lasers.

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30 At the collision energies of our experiment no vibrational excitation of the NO fragment
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32 is possible, only rotational excitation. Thus, the collection of the energetically possible NO(*J*)
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34 states provides a full record of the collisional energy transfer distribution since the dissociated
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36 NO(*J*) and O fragments are momentum-matched. While the pump laser provides a very narrow
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38 distribution of NO₂* excitation energies, there is some additional spread in the degree of NO₂*
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40 excitation due to incompletely cooled NO₂ in the beam. The nozzle-jet expansion of NO₂ in Ar
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42 resulted in a NO₂ rotational temperature of ~25K. This was determined by scanning the pump
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44 laser through the dissociation threshold for various *J*-states of NO.
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Figure 1. Schematic representation of experiment. Panel (a) shows the spatial configuration, panel (b) shows the relative energetics, and panel (c) illustrates the key velocity components of the experiment. The Newton diagram shown in panel (c) shows the velocity components of the NO fragment as emanating from the velocity vector of the inelastically scattered NO₂** molecule; the dynamics of NO₂* + Ar scattering are centered about the center-of-mass velocity, V_{COM} .

2.2. Theory

The collisional energy transfer function $P(E, E')$ for ground state NO₂ colliding with Ar was calculated using a newly fitted potential energy surface (PES) and classical trajectories. The PES for NO₂ + Ar may be written

$$V = V_{\text{NO}_2} + V_1 \quad (1)$$

where V_{NO_2} is the PES for isolated NO₂, and V_1 is the intermolecular NO₂–Ar PES. Several fitted NO₂ potential energy surfaces have appeared in the literature.⁶⁶⁻⁶⁹ A new analytic representation of V_{NO_2} was obtained here by fitting a simple functional form to the results of dynamically weighted (dw) Davidson-corrected (+Q) multireference configuration interaction (dw-MRCI+Q/CBS) calculations.^{70,71} The dw scheme included six electronic states and a range parameter of 2 eV. The (9e,7o) active space was used, and the complete basis set (CBS) limit was extrapolated via a two-point formula from the cc-pVTZ and cc-pVQZ basis sets. This

method predicts an equilibrium geometry of NO₂ that is in very good agreement with experiment,⁷² with N–O distances differing by less than 0.001 Å and an O–N–O angle differing by less than 1°. The energies of the optimized geometries produce a classical ON–O dissociation energy (25617 cm⁻¹) that is in reasonable agreement with the value inferred from experiments by Bezel et al.⁶⁴ (25128 cm⁻¹). The use of a multireference method allows for an accurate characterization of the NO₂ PES globally, including energies near the threshold for bond breaking, as demonstrated previously for CO₂.⁷³ The calculated dw-MRCI+Q/CBS energies included geometries with N–O distances varying from 0.7–5 Å and O–N–O angles varying from 45–180°. Geometries with energies above 50,000 cm⁻¹ were excluded from the data set (where the zero of energy was set to the classical equilibrium for O + NO), resulting in a final data set of 6684 geometries.

The data set was symmetrized with respect to O-atom exchange, doubling its size. These data were fit to the functional form

$$V_{\text{NO}_2} = V_{\text{NO}}(R_1) + V_{\text{NO}}(R_2) + \sum_{i,j,k} \ddot{a} c_{ijk} x_1^i x_2^j x_3^k, \quad (2)$$

where R_1 and R_2 are the two N–O distances, V_{NO} is a one-dimensional NO PES, R_3 is the O–O distance,

$$x_a = \exp(-R_a), \quad (3)$$

$i,j,k = 0-7$, and the 343 linear coefficients c_{ijk} were determined via a weighted least-squares minimization. Geometries with energies below -15000 cm⁻¹ were weighted more heavily than the other data. The mean unsigned error over the entire data set was 750 cm⁻¹, and the mean unsigned error for data with energies below -15000 cm⁻¹ was 210 cm⁻¹. The equilibrium structure for NO₂ on the fitted surface is within 0.002 Å and 0.2° of the experimental values, with a classical dissociation energy of 25734 cm⁻¹. Calculated rotational constants for the fitted surface (7.95, 0.439, 0.416 cm⁻¹) are in excellent agreement with experiment⁷² (8.00, 0.433, 0.410 cm⁻¹). Agreement is also good for the fitted (809, 1404, 1581 cm⁻¹) and experimental harmonic frequencies⁷² (750, 1318, 1618 cm⁻¹).

The “separable pairwise” approximation was used for V_I , where

$$V_I = \sum_a A_a \exp(-R_a / B_a) - (C_a^6 / (R_a^6 + D_a^6)), \quad (4)$$

and the index a labels the three intermolecular pairs of atoms (the Ar–N and the two Ar–O distances). The eight unique adjustable parameters in eq 4 (the same parameters were used for both Ar–O interactions) were fit to 169 counterpoise corrected QCISD(T)/CBS energies for $\text{NO}_2 + \text{Ar}$, where the CBS limit was estimated using a two-point formula with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, with a mean unsigned error of 10 cm^{-1} . For fixed NO_2 –Ar orientations, the local minima in the interaction energies vary from -90 to -180 cm^{-1} and the Ar–N distances associated with these minima vary from 3.4 – $4.6 \text{ \AA}$. This anisotropy and the anisotropy of V_1 at shorter, repulsive distances are well reproduced in the fitted surface. As demonstrated by numerous classical trajectory studies[46,49-52,74,75], energy transfer is most sensitive to the repulsive part of V_1 and is relatively insensitive to the PES of the target species (V_{NO_2}). The present PES fitting strategy has been validated using full-dimensional direct dynamics trajectories[60,76], and has been used in quantitative dynamical studies where the results are expected to depend sensitively on V_1 , including predictions of the unimolecular kinetics of CH_4 and $\text{C}_2\text{H}_3 + \text{He}$ [62] and predictions of dilute gas diffusion coefficients for several n-alkanes + N_2 . [77]

$\text{NO}_2 + \text{Ar}$ collisions were simulated using classical trajectories where the initial vibrational (and total) energy of NO_2 , E' , was set to 97% of the classical dissociation energy with no initial rotational energy, $J' = 0$. The initial coordinates and momenta were obtained for the E', J' microcanonical ensemble by sampling uniformly from separate long-time trajectories for isolated NO_2 . The relative collision energy for each trajectory was selected from a Gaussian distribution with a center at 560 cm^{-1} and a width parameter of 60 cm^{-1} . The impact parameter was sampled out to very long range ($b_{\text{max}} = 10 \text{ \AA}$), and the initial and final NO_2 –Ar separations were $14 \text{ \AA}$. At these large final separations, the total energy of NO_2 after the collision, E , can be calculated unambiguously, and the energy transferred in the collision is defined $\Delta E = E - E'$. We also calculated the final rotational state of NO_2 , J . The vibrational energy transferred in the collision can be defined $\Delta E_{\text{vib}} = \Delta E - B J^2$, where $B = 0.42 \text{ cm}^{-1}$ and $B J^2$ is the final classical rotational energy of NO_2 . The ensemble consisted of 120000 trajectories.

The choice of initial vibrational energy in the trajectory calculations is further from the threshold for dissociation than in the accompanying experiments, but it avoids the complication of characterizing the final states of dissociated NO_2 . We tested the sensitivity of our calculated results to the choice of E' (where E' was set instead to 91% or 94% of the dissociation energy)

and for ensembles where J' was selected from a classical thermal distribution with a rotational temperature of 15 K. The results of these tests agreed quantitatively with the results presented here.

3. Results and Discussion

In order to determine the shape of the collisional energy transfer probability distribution, $P(E, E')$, we measure the velocity distribution of the NO fragments that result from collisions that have sufficient energy to produce different rotational states of the NO. From the velocity of these fragments and knowledge about how the collisionally excited NO_2^{**} molecule dissociates when excited to a particular energy we are able to extract from the data the shape of the original collisional energy transfer probability distribution between the NO_2^* and the Ar.

The following three-step mechanism describes the collisional induced dissociation processes. The related energies are depicted in Figure 2.

The first step is a photoexcitation of ground state NO_2 to internally vibrationally excited state, NO_2^* , with an energy denoted E_{int} . The second step represents an inelastic scattering event that increases the internal energy of the NO_2^* to a value by an amount denoted E_{txfr} above the dissociation threshold; the conversion of kinetic to internal energy produces an $\text{NO}_2^{**} + \text{Ar}$ system with a reduced total kinetic energy denoted as E_{trans} . The final process represents the unimolecular dissociation of the NO_2^{**} molecule to specific rotational states of NO with associated kinetic energy releases, denoted E_{recoil} , that are determined by the rotational energy, E_{rot} , and the inelasticity of the collision (step 2). The relationship of these energies is described in detail below to explain how the NO velocity distribution provides a direct metric of the collisional energy transfer probability distribution. This three step mechanism contains within it the assumption that the Ar atom does not participate in the NO_2^{**} dissociation event. We will examine this assumption below.

The principles of conservation of energy and momentum underpin the analysis of the NO images. The distribution of NO velocities is related to the system energetics as shown in Figure 2. In this experiment what is measured is the velocity distribution of a particular $\text{NO}(J)$ rotational

state, and due to the knowledge of all the other terms, this velocity distribution is directly related to the $\text{NO}_2 + \text{Ar}$ collisional energy transfer distribution. As illustrated in Figure 2, the NO fragment velocities are a vector sum of two components: the NO_2^{**} “translation” velocities (i.e., the velocity of the NO_2^{**} molecule after the collision that together with the Ar collision partner constitutes the kinetic energy that was not converted to internal energy) and the “recoil” velocity, which is from the portion of the excess energy in NO_2^{**} above the dissociation threshold that results in NO and O kinetic energy release. By analysis of the energy relationships we see that the magnitudes of the recoil and “translational” velocities are interrelated at a given $\text{NO}(J)$ rotational state.

Figure 2. Schematic representation of energy and momentum conservation approach of experiment. See text for definition of terms, and online edition for references to color. The distribution of energies transferred from kinetic to internal energy of NO_2 , E_{txfr} , is determined by the measurement of the NO velocity distribution and rotational state. The NO velocity is a vector sum of two components, the recoil velocity from the NO_2^{**} dissociation event and the velocity of the NO_2^{**} that comes from the unused “translational” kinetic energy of the $\text{NO}_2 + \text{Ar}$ system. The inelastically scattered NO_2^{**} molecule undergoing dissociation is shown as forward-scattered, where in the experiment the red (dashed-line) recoil “rings” of v_{recoil} can emanate from all possible positions on the correlated black (dotted-line) “origin” set by v_{trans} . Note that for a given amount of collisional excitation in NO_2^{**} , v_{recoil} is reduced by the NO rotational energy.

A series of energy relationships constrain the energy available for NO + O kinetic energy release (E_{recoil}). As shown in the schematic of Fig. 2, the total energy of the system (E_{tot}) is the sum of the internal energy of the vibrationally excited NO₂* molecule (E_{int}) and the collision energy (E_{coll}).

$$E_{\text{tot}} = E_{\text{int}} + E_{\text{coll}} \quad (8)$$

The internal energy (E_{int}) of the NO₂* molecule is set by the λ_{pump} and is accurately and precisely measured, the collision energy E_{coll} is set by the beam velocities and is accurately determined with a known distribution. The unknown, E_{txfr} , is the amount of energy available in the collision that is removed from the total kinetic energy of the collision partners and transferred to the internal degrees of freedom of the NO₂* to form NO₂**. This E_{txfr} distribution is shown schematically by the exponential decay function at an energy of E_{int} . For illustration, a single E_{txfr} value is shown schematically and the remaining energies (except E_{diss} , the known NO₂ dissociation energy) are referenced to this quantity. A given value of E_{txfr} leaves a given amount of “translational” kinetic energy (E_{trans}) in the system corresponding to the remaining collision energy that was not used to increase the internal energy of NO₂* to make NO₂**.

$$E_{\text{txfr}} = E_{\text{coll}} - E_{\text{trans}} \quad (9)$$

Of the E_{txfr} energy that is input into the NO₂** system, a certain amount is required to push the NO₂* molecule above the dissociation threshold, and only the excess energy E_{avail} is available for the NO and O fragments. The available energy E_{avail} is a function of the difference between the internal energy of the NO₂** and the NO₂ dissociation energy, i.e.,

$$E_{\text{avail}} = E_{\text{txfr}} - (E_{\text{diss}} - E_{\text{int}}). \quad (10)$$

Since there is insufficient energy available from the collision to generate NO vibrational excitation, the energy available to the NO + O fragments (E_{avail}) is the sum of the NO rotational energy, E_{rot} , and the NO + O kinetic energy release, E_{recoil} , i.e.,

$$E_{\text{recoil}} = E_{\text{avail}} - E_{\text{rot}}. \quad (11)$$

For a given VMII image of a particular NO(J) state the rotational energy is fixed. Thus, the distribution of NO recoil energies is determined directly from the distribution of collision energies transferred into the NO₂** internal degrees of freedom, E_{txfr} , i.e.,

$$E_{\text{txfr}} = E_{\text{recoil}} + E_{\text{rot}} + (E_{\text{diss}} - E_{\text{int}}). \quad (12)$$

The experiment measures fragment velocities that are fixed by the energy constraints above as well as the conservation of momentum. While only the NO fragment velocity is measured, this is sufficient to fix the velocity of the O co-fragment, and thus the E_{recoil} distribution is uniquely related to the NO recoil velocity distribution. As shown in the NO(J) velocity schematic of Figure 2, the total NO velocity distribution is a vector sum of this NO recoil velocity v_{recoil} and the “translational” NO velocity, v_{trans} , which is the scattered NO₂** velocity. If the collision between the NO₂* and Ar is purely elastic, the NO₂* does not dissociate and the magnitude of the “translational” velocity is determined by the full E_{coll} value. The conversion of available collision energy, E_{coll} , to internal energy reduces the “translational” velocity by an amount determined by the degree of internal energy excitation, E_{txfr} . This reduction in v_{trans} is accompanied by a concomitant increase in v_{recoil} , however, this NO recoil velocity is reduced by the degree of rotational excitation in the NO fragment, E_{rot} . With this full accounting between the measured, known, and unknown quantities of the experiment established, our approach is to image the NO velocity distribution of a range of rotational states and analyze these VMII images through comparison to a model with only one adjustable parameter, the collisional energy transfer distribution E_{txfr} . The shape of the energy transfer function over the energy range any one particular rotational state of the NO is sensitive to will be assumed to be exponential. As each rotational state is sensitive to different regions of excitation energy we will find the best exponential fit for each sub region of energy transferred.

The velocity distribution of the NO CID products is quantified by rotational-state-selective VMII. Images were acquired for a series of energetically-accessible NO(J) fragments, specifically $J = 0.5, 1.5, 3.5, 5.5, 6.5$ and 7.5 . The raw images of these rotational quantum states are shown in Figure 3, overlaid by the elastic scattering velocity radius. A few trends are apparent in these images. It is immediately apparent that the clear velocity “rings” of typical inelastic scattering experiments are highly “smeared” by the NO recoil distribution. A clear relationship between the width of the NO velocity distribution and the rotational state is apparent in the images and we investigate the origin of this trend.

Figure 3. Raw images of velocity distributions from select NO(J) states. NO molecules are produced from collisional dissociation resulting from $\text{NO}_2^* + \text{Ar}$ inelastic scattering. NO_2^* forward scattering is shown at the vertical position. The outer white circle shows the elastic scattering radius for NO_2 and the inner white circle shows the reduction of velocity equivalent to the degree of energy required to excite the given NO(J) rotational state from the $\text{NO} + \text{O}$ dissociation threshold.

Due to the increasing degeneracy of the NO(J) states with energy, an NO_2^{**} molecule with a certain energy above the dissociation threshold is more likely to produce an energetically accessible high- J state than a low- J state. Ionization from individual NO(J) rotational states thus produce energy-dependent sensitivities which must be factored into the analysis. These propensities have been previously determined by measuring the product distribution following laser excitation to many different energy above the dissociation limit,⁶⁵ and it has been verified that these follow statistical behavior,⁷⁸ as illustrated in Figure 4. We undertook an experimental reexamination of the J -state yield as a function of energy produced by direct single-photon photodissociation of NO_2 . Measurements employing both fixed-probe scanned pump and fixed pump scanned probe (REMPI spectra) were performed and we confirmed the NO(J) distributions as a function of energy follow a simple statistical model. The details of this investigation are summarized in Fig. S1 of the Supplementary Information, and our primary conclusion is that we are able to predict the particular and unique NO(J) distribution that results from a specific above-

threshold energy in the NO_2^{**} system. The assumption inherent in this statement is that the dissociation at a particular energy of NO_2 behaves the same from laser-excited molecule (high vibrational excitation low rotational excitation) and collisionally excited molecules (both rotationally and vibrationally excited). Based upon our knowledge of the $\text{NO}(J)$ distribution as a function of energy, we can determine the energy “sensitivity” of a particular J -state image in revealing the distribution of collisionally excited energies above NO_2 dissociation threshold. As shown in the upper panel of Figure 4, these $\text{NO}(J)$ “windows” dictate how sensitive our individual J -state VMII images are to various energies in the dissociating NO_2^{**} molecule. As illustrated by the lower panel of Figure 4, due to the small degree of internal energy in our NO_2 beam, the yield of a given J -state image will also include the initial distribution of internal energies. This is because the measured collisional excitation distribution from each $\text{NO}(J)$ state is convolved with the initial thermal energy distribution in the molecular beam.

Figure 4. Energy dependence of $\text{NO}(J)$ distributions. The distributions shown in panel (a) follow a statistical model based upon the $(2J + 1)$ rotational state degeneracies, $\text{NO}(X)$ spin-orbit excited states, and available $\text{O}(^3\text{P})$ states. These state probabilities show the sensitivity of a given $\text{NO}(J)$ image to a particular degree of collisional energy excitation, and thus each J -state

dictates a sensitivity “window” into the excitation distribution. The measured collisional excitation distribution from each $\text{NO}(J)$ state is convolved with the initial thermal energy distribution in the molecular beam, as shown in panel (b).

With the particular $\text{NO}(J)$ energy dependent sensitivities in hand we can generate a model of NO J -state recoil velocity distribution that is a function of only one parameter, the best exponential shaped collisional energy transfer distribution for each NO rotational state window. Our approach is to compare the model to our experimental data in order to iteratively input the best energy transfer distribution that fits the data. Since we wish to determine the energy transfer distribution with as few assumptions as possible, a model of NO recoil as a function of NO_2 energy is made that eliminates the effect of the $\text{NO}_2 + \text{Ar}$ scattering differential cross-section (DCS). We employ a projection of each of the modeled and observed NO velocity images that describe identical quantities. Specifically, the integration of the signal in the images at a given radius, centered at the center-of-mass of the elastic scattering of the $\text{NO}_2 + \text{Ar}$ collision, around all angles generates a radial distribution function that is sensitive to the energy transfer function and insensitive to the $\text{NO}_2 + \text{Ar}$ DCS.

The generation of the NO velocity model images is illustrated in Fig. 5. Using the energy- and momentum-conservation principles outlined above, we make a lowered-dimensional model of all the possible $\text{NO}(J)$ velocities that can result from $\text{NO}_2^* + \text{Ar}$ scattering. We assume an isotropic emanation of the NO fragment, thus there is no correlation between the direction of the scattered NO_2^{**} (the NO v_{trans}) and the direction of recoil of the NO fragment (v_{recoil}), only a correlation of magnitudes. We will show below that breakdown of this assumption may be critical to explaining the discrepancy we will demonstrate between the experimental measurement of the $P(E, E')$ distribution and the calculated distribution. As shown in panel (a) of Fig. 5, we represent the NO recoil as two-dimensional circles and the NO_2^{**} scattering vector as a one-dimensional line. This reduction in dimensionality is properly accounted for in our radial distribution projection analysis, because it preserves cylindrical symmetry about the relative velocity vector of NO_2^* and Ar . The importance of this symmetry and the projection of the model and experimental images to an equivalent radial intensity distribution are described in further detail below.

The degree of loss of kinetic energy in the $\text{NO}_2^* + \text{Ar}$ system and the selection of the particular $\text{NO}(J)$ state directly determines the NO recoil velocity magnitude. As shown by the

PES schematic in Fig. 5, at each particular collisional E_{txfr} value (and for each individual NO(J) state) there is a corresponding “ring” of NO velocities which is a vector sum of the 2-D v_{recoil} (red circles) and 1-D v_{trans} (red ‘x’s). The sum of all of these possible velocities produces the example NO $J=3.5$ distribution map in the top right (panel (b)) of Fig. 5. Finally, the model is convolved with the available energy distributions; the initial degree of thermal energy in the NO₂ beam as well as the NO₂ and Ar beam velocity spreads must be accounted for in terms of the contribution to total available energy. The image in panel (c) of Fig. 5 is the result of the one-dimensional model convolved with the distribution of total available energies. Inherent in this image is that all energies of the NO₂ are equally excited (the $P(E,E')$ distribution is given as a constant with energy), and the $J=3.5$ rotational quantum state detects each of these energies with equal sensitivity (as if at all NO₂ energies above the energy of NO($J=3.5$) the NO₂ dissociates and only produces NO($J=3.5$)). We will add the energy sensitivity window, as is given by the windows discussed above, and fit a energy transfer function to each window to find the best fit to the data.

Figure 5. Construction of J -state specific NO velocity distribution model for example of $J=3.5$. As shown in panel (a), the increase in NO₂ internal energy by reduction of total [NO₂ + Ar] kinetic energy results in a fixed [NO + O] kinetic energy for a particular NO(J) state. The collection of all possible NO recoil velocities in panel (b) is “smeared” by the available energy distributions; the thermal NO₂ in the molecular beam and the beam velocity spreads result in a distribution of total available energies in the system; the resulting distribution of all possible velocities available to the NO(J) fragment is shown in panel (c).

The distribution shown in Fig. 5c assumes all energetically possible energies are equally populated and the particular J state, $J=3.5$, is equally sensitive to all energies. However, for each NO J -state there is a unique sensitivity to the various excess energies of NO₂** (*i.e.* the red ‘x’s of Fig. 5 receive different sampling weights for each J -state “window”). This involves both an energetic cut-off, as well as a decay in sensitivity with increasing energy as other higher- J “windows” become energetically accessible and “steal” population into these higher rotational states. As described above, these windows are calculated from a statistical account of the state degeneracies. To account for the observed velocity distribution of a particular NO(J) state, this statistical weighting to the energy window of a particular J state must be added to the model of Fig. 5. The results are shown in Fig. 6. Shown as an example in the upper left and right panels of Fig. 6 are the $J(1.5)$ and $J(7.5)$ energy “windows”, respectively. The results of the weighting they impose upon all possible NO recoil velocities (*i.e.* the image in panel (c) of Fig. 5) are shown in the middle velocity images of the figure. These images assume all possible energies are equally likely, $P(E,E')$ is a constant, and show only the NO $J=1.5$ and $J=7.5$ energy sensitivity of the E_{txfr} measurement. It is clear from the differences between these velocity distribution maps that the NO J -state “windows” have a strong effect on what NO₂** energies are probed.

Figure 6. Illustration of J -specific sensitivity “windows” and $P(E)$ energy transfer function weighting on modeled velocity distributions. The J -window function dictates the “instrument function” of a particular $\text{NO}(J)$ state towards all the possible NO_2 internal energies and mitigates the importance of various NO recoil velocity groups. The extents corresponding to 75% of total sensitivity are shown by the red overlay on the curves. The $P(E, E')$ distribution determines the distribution of NO_2 energies that produce NO fragments, and is represented here by a single-exponential decay function. This single-exponential $P(E, E')$ function is adjusted to fit the data for each $\text{NO}(J)$ image.

The importance of each particular E_{txfr} value (and thus the J -dependent signal from the correlated NO recoil velocity distribution) is given by the collisional energy transfer distribution,

$P(E_{\text{trf}})$, i.e., $P(E, E')$. As shown by the middle and lower panels of Fig. 6, a trial P function is input and the resulting weighting of the J -state model images is calculated. In this case, the trial function of

$$P(E, E') = \exp(-\Delta E/\alpha) \quad (13)$$

where $\alpha = 50 \text{ cm}^{-1}$ is shown for both J -states. The energy range of the $P(E, E')$ function to which the particular J -state image is sensitive to is shown as a thick red overlay on the $P(E, E')$ curve. To preserve the straightforward nature of our approach, we model the $P(E, E')$ function for each J -state image as a single exponential decay function, and thus fit the model to the data with a single numerical parameter. This decay constant, α , represents the single adjustable parameter of our model, and it is clear from the images in the lower panels of Fig. 6 that there is a strong effect on the modeled NO velocity distribution from introducing this $P(E, E')$ weighting.

As stated previously, a comparison between the experimental and modeled velocity distributions requires collapsing the images into an image projection that the two share in common. One such projection is the radial distribution of the angle-integrated signal about the center of mass of the $\text{NO}_2^* + \text{Ar}$ system (as shown by v_{COM} in Fig. 1(c)). This annular integration allows the effect of the $\text{NO}_2^* + \text{Ar}$ DCS to be ignored and represented by the 1-D model of NO_2^{**} scattering. (An example justification of this is shown in Fig. S2 of the Supporting Information.) In order to compare with the experimental data, an image transform, inverse Abel transform, is required before angle-integration and comparison to the model because the experimental image represents a 3-D velocity distribution “crushed” onto a 2-D surface. Our images have cylindrical symmetry about the relative $\text{NO}_2^* + \text{Ar}$ velocity vector. For images with this symmetry property, this problem has been previously investigated in detail and we employ the BASEX program of Reisler and co-workers⁷⁹ to perform this inverse Abel-transform. This transform essentially outputs the 2-D basis of the 3-D image, and thus the radial distribution of the image is a direct representation of the magnitudes of the velocity distribution (*i.e.* NO speeds). The “raw” experimental images are inverse-Abel transformed and integrated annularly to produce an experimental radial distribution that can be directly compared to the simulated radial distribution of the model, these are shown in Fig. 7.

In Fig. 7 is a direct comparison of the radial velocity distribution of the data and the model for each J -state for different α parameters for the $P(E, E')$ trial input. The comparison between data and experiment is used as a basis for an error minimization routine that yields the

best fit single-exponential energy transfer function decay parameter α for each J -state. Since the energy “window” for production of a particular NO J -state from NO₂** has a defined range, this essentially gives the average slope of the $\log(P(E,E'))$ function over this energy range. The best single-exponential fit to each J -state velocity map image is not the same, and follows a rough increasing trend with energy. The change in the best-fit α value means that the measured collisional energy transfer distribution is best described by a multi-exponential decay.

Figure 7. The radial intensity distribution of the NO signal is inverse-Abel transformed and integrated around all scattering angles in order to eliminate the effect of the NO₂ + Ar DCS from the analysis. A comparison of the radial intensity distribution from the experimental images to that of the NO recoil model is shown for all the studied NO(J) states. The comparison shows the best fit single-exponential $P(E,E')$ function is shown for each J -state, as well as a consistent set of lower and upper bound $P(E,E')$ trial functions. The error of model vs. data is shown in the lower panels.

The overall behavior of the experimental $P(E,E')$ distribution over the energy range investigated is summarized in the lower panel of Fig 8. The best-fit single-exponential parameter is plotted vs. the position and extent of the energy “window” each NO(J) state provides into the ΔE (E_{txfr}) NO₂** excitation. These best-fit single-exponential decay parameters for each of the J -states are $\alpha = 34, 30, 22, 27, 52$, and 80 cm^{-1} for $J = 0.5, 1.5, 3.5, 5.5, 6.5$ and 7.5 , respectively.

Also shown is the single-exponential fit ($\alpha = 125 \text{ cm}^{-1}$) of the study of Sanov et al.³⁷ who considered a wider and higher energy range. Shown in the upper panel of Fig. 8 are the results of the trajectory calculations over the experimentally-relevant energy range. The multi-exponential behavior of the calculated $P(E, E')$ distribution is immediately apparent. A comparison to the experimental data shows obvious qualitative agreement and rough quantitative agreement. The best single-exponential representation of the calculated $P(E, E')$ curve over the energy region interrogated by the low- J images is with a decay parameter $\alpha = 20 \text{ cm}^{-1}$, which agrees well with the experiment. The approximate single-exponential representation of $P(E, E')$ over the higher- J state energy region of the experiment is in the range of 100–300 cm^{-1} , in rough agreement with the current study and the previous work of Sanov et al.³⁷

Figure 8. A comparison of experimentally-determined and calculated $P(E,E')$ distributions. The trajectory $P(E,E')$ results are shown in the upper panel, and the numerical derivative of this distribution is comparable to the single-exponential fits, and shown as a dotted line in the lower panel. The best fit single-exponential $P(E,E')$ function is shown in the lower panel for each J -state as the vertical position of a horizontal line. The open circle shows the “center-of-mass” of the J -state’s “window”, and the length of the line corresponds to the extent of that particular J -state “window” used to interrogate the NO_2 $P(E,E')$. Also shown is the experimental result from a previous experimental study of Sanov et al., with the corresponding energy range that was interrogated. The current study clearly shows a multi-exponential $P(E,E')$ shape, in qualitative agreement with the calculations.

Despite the qualitative agreement between the experimental result for the $P(E,E')$ behavior and the QCT trajectory results, there is clear quantitative discrepancy. The experimental approach is to report a best-fit characterization of the real $P(E,E')$ over the energy sensitivity of a particular $\text{NO}(J)$ image. As a check on comparison between the trajectory calculations and the experiment we have taken the $P(E,E')$ as determined by the QCT and predicted the velocity

distributions that we would see in the experiment for each rotational quantum state of the NO molecule. The $P(E,E')$ determined by the QCT is used to generate the model image as shown in the lower panels of Fig. 6. These images are compared to the experimental images using the radial integration projection and the results of this comparison are shown in Fig 9. The comparison of the experimental and QCT results shows that the experimental results do indeed show a lower $P(E,E')$ relative to the QCT calculations. We note that by inspection of Fig. 8 we see that the fits are closest for the low J values that sample the “first exponential” decay and the highest J level measured, $J=7.5$, which is sensitive mainly to the “second exponential” decay and the fits are worst in the transition region where a single exponential fit is a poor representation of the calculated $P(E,E')$ curve. It is not entirely clear how to reconcile this poor quantitative agreement.

Figure 9. A comparison of the experimental and modeled radial intensity distributions using the QCT $P(E)$ for each the studied NO(J) states. The comparison shows the data, the best fit single-exponential $P(E)$ function, and the the result of the $P(E)_{\text{QCT}}$.

A variety of sources were considered for the quantitative disagreement between the experimental and calculated results. There are assumptions in both the trajectory calculations and

experimental analysis that may lead to this discrepancy. The possibility exists that the experiment is biased towards the detection of certain types of energy transfer, in that there is a fundamental assumption of statistical dissociation dynamics from NO_2^{**} to make the distribution of $\text{NO}(\text{J})$ states. While we verified the statistical distribution of $\text{NO}(\text{J})$ states from NO_2^{**} molecules prepared by direct photodissociation, we do not directly do so for the $\text{NO}(\text{J})$ distribution produced from CID, but rather assume the statistical behavior as an underpinning of our analysis. Another possibility is that the presence of the NO_2 electronic excited state may significantly affect the energy transfer process, which was modeled only with the ground state manifold of internal states.

Finally, any effect that created a non-isotropic dissociation of the NO_2^{**} creating a non-isotropic distribution NO products would affect our analysis and fitting. Two possible effects were investigated that could cause a non-isotropic NO distribution. First, if the collisional excitation of NO_2^* to high internal energies is a non-isotropic event and the highly excited NO_2^{**} fell apart before it had a chance to rotate and randomize its position then the resulting distribution of NO would be non-isotropic. Second, if the assumption that the collision event is temporally distinguishable from the unimolecular dissociation due to the rapidity of the scattering event is incorrect and some fraction of the quickly dissociating NO_2^{**} molecules produce NO which has a subsequent collision (either elastic but direction changing or inelastic) with the Ar atom that excited the NO_2^* , then a non-isotropic NO distribution would be formed.

To investigate the possibility of non-isotropic collisional excitation of NO_2^* , we analyzed the ensemble of trajectories used to generate figure 8. For each trajectory in the ensemble, the smallest of the two Ar-N-O angles, θ_{ArNO} , was calculated at the “impact geometry,” defined here as the geometry along the trajectory with the shortest Ar-NO_2 center-of-mass distance. Figure 10 shows the fraction collisions that transfer at least 300 cm^{-1} binned as a function of θ_{ArNO} . (One could distinguish collisions that occur on the concave side of NO_2 from those on the convex side, but we do not do so in figure 10 as this distinction complicates the figure but does not affect the present conclusions.) One can see from figure 10 that low angle collisions, which correspond to Ar striking the O atom along an NO axis, are ~ 5 times less likely to transfer at least 300 cm^{-1} than collisions where Ar strikes an NO axis at angles between 25 and 65° . Above 65° the likelihood of energetic collisions declines, where angles near 130° correspond to Ar striking NO_2 along its C_{2v} axis. Figure 10 thus demonstrates non-isotropic excitation for high-energy

collisions. Similar distributions may be obtained for cutoffs larger than 300 cm^{-1} , while the distribution necessarily approaches an isotropic one as the cutoff is lowered to include all collision outcomes.

Figure 10. The fraction of collisions that transfer at least 300 cm^{-1} of energy as a function of θ_{ArNO} . The results are shown binned with respect to θ_{ArNO} , with a bin size of 10° .

As the rotational constants of NO_2 are small and NO_2 is initially rotationally cold, it takes several picoseconds, depending upon the exact rotational excitation, for NO_2 to rotate. If the dissociation of NO_2 is fast on this time scale, then the angular distribution of the NO product fragment may reflect this excitation anisotropy. The trajectory results indicate that the degree of anisotropy should increase with increasing excitation, which, on average, also results in faster dissociation rates for NO_2 . The presence of non-isotropic scattering of NO may therefore have a quantifiable effect on the present analysis, particularly for large ΔE . A second related effect might further complicate the present interpretation. If one assumes that NO_2 dissociation along the center-of-mass vector of O–NO vector is fast enough to occur while Ar is still interacting with NO_2 , it is instructive to correlate the angle of the departing NO fragment with θ_{ArNO} . On average, the distance of closest Ar– NO_2 approach is $\sim 3\text{ \AA}$, and using this distance one calculates

that the departing NO fragment would be directed toward Ar for $\theta_{\text{ArNO}} \approx 35^\circ$. Notably, this value of θ_{ArNO} is close to the peak in the distribution of energetic collisions shown in figure 10. Assuming fast dissociation, energetic collisions are therefore more likely to dissociate in such a way as to interact with Ar. Therefore it is quite reasonable that some fraction of the dissociating NO molecules will feel the presence of the Ar atom either while dissociating or with as a subsequent collision after dissociation, particularly for energetic collisions as these collisions necessarily result in slowly moving Ar atoms. Such events may be observed via classical simulations, but we do not attempt to quantify them here as: (1) the present potential energy surfaces do not include reliable Ar–O or Ar–NO interactions, and (2) classical mechanics is likely not suitable for modeling such threshold dissociation events. However, due to the fast dissociation rates reported elsewhere⁸⁰ for NO_2^{**} , interactions may be possible such that the kinetic energies of the NO + O dissociative recoil are perturbed by the Ar collider. If the present reaction were considered in the reverse direction, such a situation may be considered a “three body” collision. Both of the effects identified here would have the result of diminishing the most forward scattered experimental trajectories thereby narrowing the experimental velocity distribution of Figures 7 and 9 making it appear that less energy has been transferred by the Ar- NO_2 collision. Neither of these velocity changing mechanisms would effect the results of the Reisler group as they did not extract the $P(E,E')$ curve from the velocity distribution of the NO fragment.

Fundamentally, the analysis in Fig. 7 and the comparison in Fig. 9 demonstrates that the experimental data is certainly sensitive to the details of the $P(E,E')$ and that the $P(E,E')$ manifests distinctly multi-exponential behavior. In general, it is worth noting that the QCT calculations and the experimental results do agree in the rough slope of the $P(E,E')$ function at the most likely events, those of low energy transfer, and these show an approximate behavior of $P(E,E') = \exp(-\Delta E/20 \text{ cm}^{-1})$.

While the degree of curvature of the $P(E,E')$ curve remains open to question, the overall behavior of the QCT trajectories is representative, and thus there are some interesting implications in the overall shape of the QCT $P(E,E')$ curve that we note. Two traces are shown for the trajectory results in Fig. 8; one represents the total energy transfer in terms of internal energy of NO_2^* and the other represents only the vibrational component of this energy transfer. We note the first moment of the total energy transfer distribution ($\langle \Delta E \rangle$) is positive, but that of

the vibrational energy transfer distribution is negative. We reiterate that these are collisions of a rotationally cold but vibrationally hot molecule, and thus due to the facile interconversion of translational and rotational energies the NO_2^* molecules are, on average, *energized* by a single collision. Of course, the rotational heating is opposite the change in vibrational energy and the trend towards equilibration of the modes is consistent. However, it is worth noting the clear qualitative differences between the first collision(s) of the molecule and later collisions, where rotational and vibrational “temperatures” are similar. This emphasizes the advantage of an approach that does not average over many collisions to determine collisional energy transfer characteristics. Another detail that is clear in the trajectory calculation results is despite the overall dominance of rotational energy transfer for ΔE_{up} collisions, at low ΔE_{up} values ($< 60\text{cm}^{-1}$) the energy transfer is almost entirely due to further vibrational excitation. This may be related to the longer-range interaction for vibrational excitation and be highly sensitive to the collision partner.

4. Conclusions

Measurements of NO velocities from collisional dissociation provide sufficient information to determine the $P(E,E')$ distribution from $\text{NO}_2^* + \text{Ar}$ collisions under some simplifying assumptions about the dissociation of the NO_2 into $\text{NO} + \text{O}$. A model was successfully developed to analyze the J -state specific NO velocity distributions. A multi-exponential energy transfer distribution has been definitively measured for energy-upward collisions for the first time. This measurement qualitatively agrees with the predictions from theoretical calculations and previous experiments but not quantitatively. One very possible reason for this is that the dynamics of the NO_2 dissociation is non-isotropic and affected by the presence of the Ar atom and this would affect the energy transfer distribution we extract from the data. A more complete calculation including excited electronic states may also help bring the calculation into better agreement with the experiments. This particular experimental approach is applicable to other molecular systems with a pair of dissociation fragments where one fragment can be interrogated by rotationally-state-selective REMPI and the other fragment is monatomic, such as acetylene.

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