Direct Observation of Electronic Intramolecular Energy Transfer through a Large Energy Gap

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A double-resonance technique is used to make the first direct observation of collision-induced electronic energy transfer in a diatomic molecule through an energy gap much greater than kT (208 cm^{-1} at $T = 300$ K). Surprisingly, J specificity is observable in this transfer process which appears to follow optical-like propensity rules in spite of the large energy gap of ~ 1760 cm^{-1} between the initially populated N_2^+ A ($v' = 4$) state and the lower-lying X ($v'' = 7$) ground-state level to which it is quenched. Room-temperature helium is the collision partner.

The determination of collisional deactivation paths and rates of electronically excited diatomic molecules is necessary for understanding a wide range of phenomena from auroral emissions to laser kinetics. Information on "purely" electronic deactivation paths, as opposed to those with perturbations, and their propensity rules are very limited; there is no previous definitive observation of collision-induced electronic energy transfer (EET) over an energy gap (ΔE) much greater than the room-temperature value of kT (208 cm^{-1}), where k_B is the Boltzmann constant and T is 300 K. This Letter reports the first direct observation of collision-induced EET through an energy gap of approximately 1760 cm^{-1}. Homonuclear $^{14}N_2^+$ is the molecule studied and its Hamiltonian rigorously has no perturbing terms that can break the Born-Oppenheimer approximation and connect the electronic states of interest. Much of the past work[1-3] has focused on transfer through perturbed rovibronic levels but this type of transfer can be viewed as a form of rotational energy transfer since the levels are perturbed and form "gates" through which the energy transfer takes place.

There is no detailed theoretical treatment of collision-induced electronic energy transfer over a large energy gap. A probable reason for this is the lack of definitive experimental data to describe the transfer process. Previous[4-11] experiments used models that assumed that EET occurred over large energy gaps but could not determine the magnitude of ΔE. In fact, it could not be shown with absolute certainty that the deactivation paths were accurate. Clearly, there must be J specificity in the transfer process for ΔE to be obtained with precision. Such specificity is observable in a pump-probe experiment if the EET process occurs at a rate comparable to rotational energy transfer (RET). If RET were much faster, rotational equilibration would occur in the initially populated state and J specificity in the collision-induced EET process would not be observable. It is difficult to imagine that an EET rate over an energy gap greater than 1700 cm^{-1} would be comparable with RET to energy levels with separa-

tions of the order of 10 cm^{-1}. Indeed, from basic theoretical considerations, the size of ΔE has an important role in the well-known time-dependent Born approximation for the collision-induced transition probability,

$$P_{if} = \left| \int_{-\infty}^{\infty} \langle f | U | i \rangle \exp(i\Delta\omega t)\,dt \right|^2 / \hbar^2, \tag{1}$$

where $\Delta\omega = \Delta E/\hbar$ and U is the time-dependent intermolecular potential. For large ΔE, the short-range repulsive portion of the intermolecular potential is expected[12] to be dominant since this is where the transition matrix element is supposed to have Fourier components with the large frequency, $\Delta\omega$. When the energy gap is small, however, the long-range attractive portion of the interaction becomes important and usually produces a cross section which is in general much larger than the case when ΔE is large.[13-15] Hence, in a double-resonance experiment, the observation of J specificity in an EET process through a large energy gap would be surprising since it would show that the EET rate is comparable to that for RET.

Recent work[16] on the collisional transfer between the N_2^+ A $^2\Pi_{ui}$ ($v' = 4$) and the X $^2\Sigma_g^+$ ($v'' = 8$) rotational manifolds where $v'' = 8$ is higher in energy but within kT of $v' = 4$ showed that collisional transfer had a propensity towards $\Delta J \approx 0$ rather than $\Delta E \approx 0$. At the conclusion of that experiment, a probe of collision-induced EET to $v'' = 7$, which is approximately 1750–1800 cm^{-1} lower in energy than the A ($v' = 4$) level, was conducted and J specificity was unexpectedly observed. This observation forms the basis of this Letter. In a similar experiment, no collisional transfer was detected from the same A-state level to $v'' = 6$ of the ground state; the energy gap in this case is approximately 3780 cm^{-1}. The experimental setup to detect EET from N_2^+ A ($v' = 4$) to the X ($v'' = 7$) level is essentially the same as described previously.[16] A two-laser, optical-optical double resonance (OODR) technique is used to conduct the experiment. This pump-probe system consists of two dye lasers which are simultaneously pumped by

a pulsed Nd-doped yttrium aluminum garnet (Nd:YAlG) laser. The pump laser selectively populates one level of the $A\,^2\Pi_{u_i}$ rotational manifold by tuning the laser to a rovibonic transition of the $A\,^2\Pi_{u_i}-X\,^2\Sigma_g^+$ (4, 0) band of N_2^+. Any collision-induced EET from this selectively populated level to the $v'' = 7$ or 6 vibrational levels of the $X\,^2\Sigma_g^+$ ground state is detected with the probe laser by scanning the $B\,^2\Sigma_u^+-X\,^2\Sigma_g^+$ ($v' = 4$, $v'' = 7$ or 6) bands and recording the uv radiation from the B state. There will be no uv signal if there is no collisional transfer. The N_2^+ ions are formed at room temperature via Penning ionization by interacting nitrogen with helium metastable atoms downstream from a dc discharge.[17] The nitrogen partial pressure is a few microns whereas the helium pressure is kept at a few Torr to produce a sufficient metastable concentration. Room-temperature helium is the collision partner since the radiative decay curves from the A ($v' = 4$) level are sensitive to pressure changes of helium but not of nitrogen. The laser pulse duration is 20 ns.

Figures 1(a) and 1(b) show the OODR excitation spectra of the N_2^+ $B-X$(4, 7) band scanned by the probe laser with the pump laser tuned to the $Q_{11}(6.5)$ and $Q_{11}(10.5)$ lines, respectively, of the $A-X$(4, 0) band. In order to optimize the probability of observing single collision effects, the laser light pulses in these figures are coincident in time so that as the pump pulse populates the initial rotational level of the A state, the probe pulse monitors collisional transfer to the X($v'' = 7$, N'') level simultaneously during the same 20-ns time period. The helium pressure is 4 Torr. The $J' = 6.5$ (f,s, −) and 10.5 (f,s, −) levels of the $A\,^2\Pi_{u\,3/2}$ rotational manifold are selectively popu-

lated by the pump laser in Figs. 1(a) and 1(b), respectively. R(6) and P(6) are enhanced in Fig. 1(a) while R(10) and the blended P(10) transitions are more pronounced in Fig. 1(b). There is selective collisional transfer to the $N'' = 6$ ($J'' = 6.5$ and 5.5) and $N'' = 10$ ($J'' = 10.5$ and 9.5) levels of the $X\,^2\Sigma_g^+$ ($v'' = 7$) state in Figs. 1(a) and 1(b), respectively. Thus, J specificity in this EET process is clearly demonstrated by the enhanced lines of these figures and it must be concluded that its rate is comparable to RET in the A ($v' = 4$) rotational manifold.

What appears to be happening is a very complex kinetic process; the initially populated A ($v' = 4$, J') level is relaxed by RET within its own vibrational manifold and by EET to the $v'' = 8$ and 7 levels of the $X\,^2\Sigma_g^+$ state. Although the effects of multiple collisions may be observable, it is most probable that the enhanced lines in Figs. 1(a) and 1(b) are due primarily to single collision effects from the initially populated J' level. Collisional transfer from the most populated A ($v' = 4$, J') level should be most effective to the X($v'' = 7$, N'') level for which it has the greatest propensity. The very remote possibility that J specificity can be observable through a relaxation path from A ($v' = 4$) to X($v'' = 8$) and finally to X($v'' = 7$) with a rate comparable to RET can be eliminated since the rotational distribution in the X($v'' = 8$) experiment[16] does not have as pronounced a J specificity as for X($v'' = 7$). The reason for this is the $v'' = 8$ rotational manifold is within kT of that for $v' = 4$ and there can be energy exchange between these two manifolds whereas $v'' = 7$ is much too low in energy relative to $v' = 4$ for this to occur. The initial J' population may also be contributing directly to the weaker rotational lines in Figs. 1(a) and 1(b), but these levels are probably more effectively populated by EET from the J' nearest-neighbor rotational levels populated by the competing RET process. The constant ratio of RET to EET rates is demonstrated by the fact that if the helium pressure is increased by a few Torr, the relative heights of the enhanced to weaker lines remain about the same provided the pump and probe pulses are coincident. If the probe pulse is delayed, however, by about 40 ns, rotational equilibration occurs most likely in the initially populated state and there is no enhancement. These enhanced lines make it possible to determine the energy gaps accurately. For example, ΔE is determined[18–20] to be 1762 cm^{-1} in Fig. 1(a). In both figures only the even, symmetric (s) levels are observed since the initially populated levels have s symmetry. If the initial state has antisymmetric (a) symmetry, only the odd, a levels are observed. Hence, the selection rule $s \leftrightarrow a$ is obeyed in this transfer process. The intensity patterns of Fig. 1 are typical of scans where the initially pumped J'(s) level has an even number $+0.5$ quantum number.
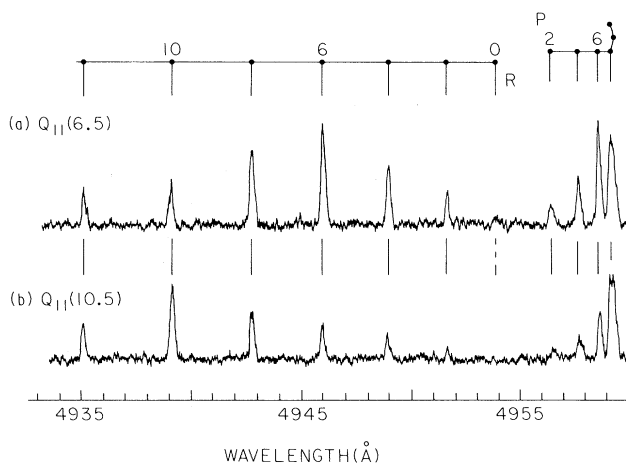

FIG. 1. OODR excitation spectra of the N_2^+ $B-X$(4, 7) band with the pump laser tuned to the (a) $Q_{11}(6.5)$ and (b) $Q_{11}(10.5)$ lines of the $A-X$(4, 0) band. The helium pressure is approximately 4 Torr.

Figure 2 shows the pattern when $J'(s)$ is an odd number $+0.5$. For this figure, the pump laser is tuned to the $P_{11}(8.5)$ line of the $A-X(4,0)$ band and the probe laser, as in Fig. 1, scans the $N_2^+ B-X(4,7)$ band. The $J' = 7.5$ $(e,s, -)$ level is selectively populated and although it is only one rotational quantum more than that for Fig. 1(a), the intensity pattern for Fig. 2 is quite different. There is a two-line maximum and the rotational lines close to the two intense lines have relatively large intensities. Thus, from the model described above, the propensity for collisional transfer from $J' = 7.5$ is not to a single N'' level but to $N'' = 6$ and 8 and its transfer probability is not as large as those in Fig. 1. If the pump laser is tuned to $J' = 5.5$, the two-line maximum shifts to $N'' = 4$ and 6.

These collisional transfers appear to follow optical-like propensity rules. The rotational constants and spin-orbit splitting of the $A\,^2\Pi_{u i}(v' = 4)$ state are known[18] and have been used to calculate[21] optical intensity relations from the initially populated levels in Figs. 1 and 2. According to the calculations and the selection rule $s \leftrightarrow a$, there is only one strong optical transition from $J' = 6.5$ (s) and that is the $Q_{11}(6.5)$ line to the $N'' = 6$, $J'' = 6.5$ (s) level. There is a nearly coincident but weak $R_{12}(5.5)$ line to the $N'' = 6$, $J'' = 5.5$ (s) level with one-fourth the intensity as the Q_{11} line. $J'' = 5.5$ and 6.5 are the two nearly degenerate spin components of the $X(v'' = 7, N'' = 6)$ rotational level; they are indistinguishable in our experiment. The weakest transition is the $P_{12}(7.5)$ line to the $N'' = 8$, $J'' = 7.5$ (s) level with about one-fifth the intensity of the $Q_{11}(6.5)$ line. Similarly, for $J' = 10.5$ (s), $Q_{11}(10.5)$ is the strongest optical line and the other transitions have much less intensity. Optical transitions from the $J' = 7.5$ (s) level, however, are of nearly equal intensity to both the $N'' = 8$ and 6 levels and consist of the $P_{11}(8.5) + Q_{12}(7.5)$ and $R_{11}(6.5)$ lines, respectively. There is, therefore, a definite
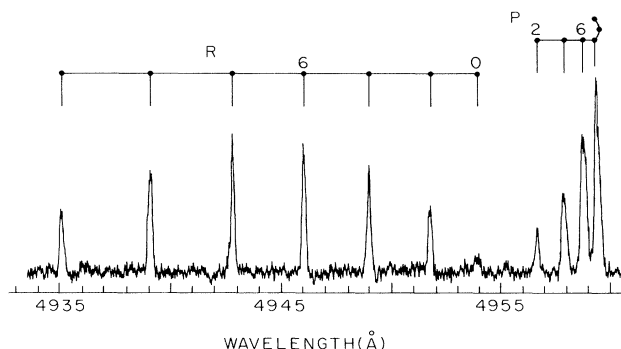

FIG. 2. OODR excitation spectrum of the N_2^+ $B-X(4,7)$ band with the pump laser tuned to the $P_{11}(8.5)$ line of the $A-X(4,0)$ band. The pump and probe lasers are coincident in time. The helium pressure is about 4 Torr.

correlation between the strong optical transitions and the collisional EET results. In Figs. 1(a) and 1(b) only one strong optical transition is expected and there is clearly one enhanced line due to collisional transfer. As discussed above, the weaker lines are probably due to the competing RET process in the initially populated state. In Fig. 2 there is not one but two enhanced lines. Also, the two-line maximum is not as pronounced as the enhanced lines in Fig. 1. In terms of the optical analogy which predicts two strong lines for this case, the optical transition probability to each of the two N'' levels is not as large as that for the Q_{11} transition applicable to Fig. 1. More importantly, the initial population is transferred into two rather than one level and therefore the results will not be as pronounced. Thus, for Fig. 2, RET in the initial state will have a greater influence and the two lines will not be dramatically enhanced. If the pump laser is tuned to $J' = 5.5$, then the optical calculations predict that the two-line maximum in Fig. 2 will shift to $R(4)$ and $R(6)$; as stated above this has been observed. Hence, the experimental data indicate that the collisional EET process has optical-like propensity rules including $s \leftrightarrow a$.

It has been shown by the observation of J specificity, that the collision-induced EET rate of quenching the $N_2^+ A (v' = 4, J')$ level to the $X\,^2\Sigma_g^+ (v'' = 7, N'')$ rotational level by helium atoms is comparable to that for RET in the $A (v' = 4)$ state. Although the cross section for this EET process cannot be determined accurately, it has been estimated previously[6] to be approximately 2 Å.[2] This unexpected result for such a large energy gap may be related to the optical-like propensity rules of the EET process. If indeed the transfer is due to a collision-induced electric dipole transition as it appears to be, then the collisional transfer probability of Eq. (1) would depend on whether its matrix element is "allowed" or "forbidden" as well as on the magnitude of the energy gap. There would need to be a balancing of these two factors. The EET process is electric-dipole allowed although its energy gap is large. RET which is much better understood[22] is dipole forbidden in this case but its energy gap is small. Thus these two conflicting factors may result in comparable probabilities for the two competing processes. The ion-induced dipole force would facilitate these processes compared to a neutral atom-molecule interaction, and it would be interesting to see how general these results become when more, direct experimental data is obtained for collisional EET over large energy gaps.

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