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Nonadiabatic transitions in the exit channel of atom-molecule collisions: Fine-structure branching in Na+N₂

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We study Na+N₂ collisions by laser excitation of the collision complex in a differential scattering experiment. The measured relative population of the Na(3*p*) fine-structure levels reflects the nonadiabatic transitions occurring in the exit channel of the collision. Theoretical results obtained with a classical-path formalism and accurate quantum chemical data for NaN₂ are found to be in good agreement. The presence of a conical intersection for the T-shaped geometry has a profound influence on the observed fine-structure branching. © 2004 American Institute of Physics.

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I. INTRODUCTION

Nonadiabatic transitions play a central role in many collisions of atoms and molecules in degenerate or excited states. The transitions between electronic states occurring in the entrance channel of a collision at large distance can be of decisive importance for the subsequent pathway of the process; this may even cover the possible outcomes of chemical reactions.^{1,2} Nonadiabatic transitions are often observed in standard scattering experiments. In this case, the experimental data usually reflect the combined action of different collisional mechanisms. The isolated study of elementary nonadiabatic events has been achieved by the optical excitation of collision pairs.^{3,4} In combination with beam techniques, experiments with well-defined kinematic and energetic conditions have become possible.⁵ We report here a differential scattering study of the process

where the frequency ν of the photon is detuned from the atomic 3*s*-3*p* resonances. In this way only the collisional complex can be excited. Nonadiabatic interactions induced by the spin-orbit coupling in the exit channel of the collision lead to the population of both the ²*P*_{1/2} and ²*P*_{3/2} fine-structure levels. Their measurement thereby permits a direct study of nonadiabatic transitions. Compared to earlier preliminary experiments,⁶ we used here a thermal N₂ beam, providing a better knowledge of the target temperature and velocity. Related to these preliminary data, Jungen *et al.*⁷ presented a surface hopping treatment of the nonadiabatic process based on CEPA (coupled electron pairs approximation) potentials. The present classical path approach uses potentials obtained with the coupled-cluster method.⁸ We achieve a very good agreement between experiment and theory and a straightforward understanding of the nonadiabatic mechanism.

II. EXPERIMENT

The experimental setup^{9,10} consists of the two particle beams, the laser beam for the excitation of the collision pairs, and the differential detection system, see Fig. 1. As the first step of the detection procedure, the excited atomic collision products are transferred to a Rydberg state by a second laser,

with $n=25$ for positive and $n=33$ for negative detuning. The Rydberg atoms are finally counted in a rotatable detector, using field ionization and single particle detection. The transfer to a Rydberg state serves to stabilize the excited Na atoms, which otherwise would decay to the ground state before reaching the detector. The procedure permits to measure the population of the two fine-structure levels by tuning the detection laser to a corresponding transition. Relative population data obtained in this way are very accurate, see Ref. 11. The only possible source of systematic errors is minor uncertainties in the subtraction of background signals. Fine-structure changing secondary collisions which occur usually in gas cell optical collision experiments are without importance due to the considerably lower gas target density. The Na beam has a thermal velocity distribution. However, we determine the Na atom velocity after the collision by a time-of-flight measurement. Neglecting rotational energy transfer, this yields kinematic information equivalent to an experiment in which the initial Na atoms have a well-defined velocity. A possible rotational energy transfer was studied by model calculations as well as by separate experiments, in which a time-of-flight analysis was applied to the Na atoms also before the collisions. Both approaches show no significant energy transfer justifying the procedure used for the kinematic analysis. Our first experiments⁶ were carried out with a supersonic N₂ beam without carrier gas. Beams produced in this way turned out to have no well-defined velocity distribution. We are now working with a thermal target gas beam, therefore. The relative kinetic energy ϵ of the collision

FIG. 1. The principle of the experimental setup with two particle beams, two laser beams, and a rotatable differential detector.

is determined with an accuracy of $\pm 20\text{--}30\text{ cm}^{-1}$, and is experimentally resolved within $\pm 5\%$. Experimental results for the fraction $p_{1/2}$ of the excited $\text{Na}(3p)^2P_j$ atoms found in the $j=1/2$ state are shown in Figs. 2 and 3. The error bars represent $\pm$ one standard deviation of the counting statistics. The systematic error is expected to be smaller than 0.01. The data are plotted vs the relative kinetic energy $\epsilon_f = \epsilon + \Delta$ after the collision. We characterize the laser frequency by the detuning $\Delta = (\nu - \nu_{\text{res}})/c$, where ν_{res} is the $\text{Na}(3s)^2S_{1/2} - (3p)^2P_{1/2}$ transition frequency. Measurements were carried out for two different detunings, 240 cm^{-1} and -179 cm^{-1} . The scattering angle was fixed: $\theta_{\text{lab}} = 18.9^\circ$ for the $\Delta = 240\text{ cm}^{-1}$ data and $\theta_{\text{lab}} = 10.8^\circ$ for $\Delta = -179\text{ cm}^{-1}$.

III. CLASSICAL-PATH THEORY OF FINE-STRUCTURE TRANSITIONS IN ATOM-MOLECULE COLLISIONS

We apply the classical-path formalism to fine-structure transitions in the $3p$ manifold of the NaN_2 collision complex. With the time-dependent Schrödinger equation and an expansion of the electronic wave function in a set of basis functions $|jm\rangle$ the equations for the amplitudes c_{jm} are of the form

$$i\hbar \frac{dc_{jm}}{dt} = \sum_{j',m'} H^{el}[\mathbf{R}(t), \mathbf{r}(t)]_{jm,j'm'} c_{j'm'} \quad (1)$$

FIG. 2. Experimental (symbols) and theoretical (line) results for the fine-structure branching for red detuning, $\Delta = -179\text{ cm}^{-1}$. The data are plotted vs the collision energy $\epsilon_f = \epsilon + \Delta$ in the exit channel. The theoretical results were obtained with the classical-path formalism. For the Monte Carlo averaging the rotational temperature of the N_2 molecules is 290 K .

FIG. 3. Experimental (symbols) and theoretical (full line) results for the fine-structure branching for blue detuning, $\Delta = 240\text{ cm}^{-1}$. For details see Fig. 2. The effect of low rotational temperature (10 K) is shown by the broken line.

The electronic Hamiltonian H^{el} in Eq. (1) is the sum of diabaticized electronic potential surfaces and the spin-orbit coupling. Its time dependence enters through the internal coordinates R and θ and the orientation of the molecular frame of the NaN_2 system. Here $R = |\mathbf{R}|$ and θ is the angle between the vector $\mathbf{R}$ pointing from the N_2 center to the Na atom and the axis $\mathbf{r}$ of the N_2 molecule. Classical trajectories are used to describe the motion of the nuclei. Explicitly we consider in H^{el} the potentials H_{xx} , H_{yy} , H_{zz} , and an interaction term H_{xz} related to a diabatic set of Cartesian orbitals $|x\rangle, |y\rangle, |z\rangle$ which describes the $3p$ manifold of the NaN_2 system in the molecular frame. The diabatic potential matrix was obtained recently by Spelsberg *et al.*⁸ in a study parallel to this investigation and represents the state of the art in present quantum chemical calculations. Figure 4 shows the potentials for the $3p$ manifold and for the ground state for the T-shaped geom-

FIG. 4. The Spelsberg-Meyer NaN_2 potentials for the T-shaped geometry.

FIG. 5. Enlarged picture of the $3p$ potentials in the interaction region for collinear arrangement. Also shown are the adiabatic potentials (dashed lines) resulting from inclusion of the spin-orbit interaction. R is the distance between the Na atom and the center of the N_2 molecule.

etry of the collisional molecule. The instantaneous orientation of the rotating molecular frame is given by a 3×3 rotation matrix

$$\begin{aligned} \mathcal{R} &= (\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z), \quad \mathbf{e}_z = \hat{\mathbf{R}}, \quad \mathbf{e}_x = (\hat{\mathbf{r}} - \cos \theta \hat{\mathbf{R}}) / \sin \theta, \\ \mathbf{e}_y &= \mathbf{e}_z \times \mathbf{e}_x, \end{aligned} \quad (2)$$

with $\hat{\mathbf{R}}$ and $\hat{\mathbf{r}}$ being unit vectors in the directions of $\mathbf{R}$ and $\mathbf{r}$, respectively. Correspondingly, we define Cartesian orbitals $|x'\rangle, |y'\rangle, |z'\rangle$ in the space-fixed frame. The electronic states $|jm\rangle$ used in Eq. (1) then follow by a constant transformation expressing the coupling of orbital and spin angular momentum

$$\begin{aligned} |m_L = \pm 1\rangle &= \mp \frac{1}{\sqrt{2}} (|x'\rangle \pm i|y'\rangle); \quad |m_L = 0\rangle = |z'\rangle, \\ |jm\rangle &= \sum_{m_L, m_S} \langle 1 \frac{1}{2} m_L m_S | jm \rangle |m_L\rangle |m_S\rangle. \end{aligned} \quad (3)$$

The states $|jm\rangle$ introduced in this way have a space-fixed projection m of electronic angular momentum $j=1/2$ and $j=3/2$ and correspond to atomic fine-structure levels in the asymptotic case. The calculation of the space-fixed potential matrix of the electronic Hamiltonian is performed by applying the transformation given by Eqs. (2) and (3) to the corresponding matrix of H^{el} in the molecular frame which is a function of R and θ only. Finally the spin-orbit coupling $V^{so} = g \mathbf{L} \cdot \mathbf{S}$ is expressed by its asymptotic form for all nuclear configurations and leads to the diagonal shifts $-g(j=1/2)$ and $g/2$ ($j=3/2$) in the representation chosen here. The adiabatic potentials obtained by diagonalization are shown for the collinear and T -shaped geometries in Figs. 5 and 6. In the space-fixed formulation of Eq. (1), Coriolis-type coupling of electronic and nuclear angular momenta is absent. By the diabatic formulation of the electronic Hamiltonian, radial and angular couplings are accounted for by the diabatic coupling term.

We use classical trajectories that switch from the ground to an excited state at a Condon point, i.e., a distance where the photon energy matches the potential difference. The relevant classical paths are determined by a search for trajec-

FIG. 6. Enlarged picture of the $3p$ potentials and the adiabatic potentials (dashed lines) for T -shaped arrangement. A crossing of the two potentials of A' symmetry occurs at 12.5 a.u. and causes a conical intersection.

ries with the scattering angle prescribed by the experiment. Alternatively, we perform a scan of the impact parameter range thus assembling the full angular dependence of the differential cross section without any need to search for specific scattering angles. The second method becomes of increasing advantage in the red wing, where the complicated deflection function often supports many trajectories with a given scattering angle. In all cases a Monte Carlo averaging over many initial conditions ($\sim 10^3$) of the molecular orientation, rotational axis, and rotational energy was performed. In this respect, the analysis is similar to the one given for the case of alignment for the excitation in atom-molecule optical collisions.¹² The distance of the atoms in the N_2 molecule is fixed at its equilibrium value in all calculations. The integration of Eq. (1) starts from the Condon point. The initial electronic state is chosen as one of the three adiabatic eigenstates of H^{el} being essentially either $2^2A'$ (blue detuning) or $1^2A'$ and $2^2A''$ (red detuning). In the latter case the two possible initial states are treated independently. Due to the small splitting of the electronic terms in the coupling and asymptotic regions compared to the present collision energies, the common-trajectory approach followed here is expected to be very reliable. Apparent fluctuations of the results are mainly of statistical nature due to the finite number of initial conditions. A small systematic error arises from ill-defined weight factors associated with certain trajectories.¹²

In Figs. 2 and 3 we show the results of the classical-path calculations corresponding to the conditions of the experiment. In another series of calculations we have investigated the dependence of the nonadiabatic transition probability on the scattering angle. In all cases we found no significant deviation from an almost constant behavior over the full range of scattering angles.

IV. DISCUSSION

For the excitation of the upper molecular state $2^2A'$ in an optical collision, the observed fraction $p_{1/2} = p(2^2A' \rightarrow 2^2P_{1/2})$ of Na^* atoms in the lower $j=1/2$ fine-structure level represents the nonadiabatic transition probability for a single passage through the coupling region. It is, therefore, more directly suited for an interpretation than probabilities

FIG. 7. Angular dependence of the nonadiabatic transition probability. The initially randomly selected orientation of the N_2 molecule with respect to the R axis is kept fixed during the collision. The probabilities are calculated for a collision energy of 650 cm^{-1} and $\Delta = 240\text{ cm}^{-1}$. The curve shows a Gaussian fitted to the data.

derived from full collisions involving in general a double passage through the interaction region. A similar interpretation holds for excitation of the other molecular states. An advantage of the present optical collision experiment is the control of the collision energy in the exit channel, $\epsilon_f = \epsilon + \Delta$.

For the following it is instructive to recall the situation occurring in optical collisions of Na with rare gases. Considering the excitation of the repulsive $B^2\Sigma$ state of the collision complex a characteristic dependence of $p_{1/2}$ on the collision energy is observed differing substantially for the lighter and heavier rare gases.^{3–5} For He and Ne, the $B^2\Sigma$ state is well above the $A^2\Pi$ state for all distances before approaching the same asymptote. In consequence, $p_{1/2}$ remains small due to preferentially adiabatic behavior on the upper adiabatic state correlating with the $j=3/2$ level of $Na(3p)$. The sudden-limit value $p_{1/2}=1/3$ arising for a fast transition through the coupling region is approached from below. The situation for the more polarizable rare gases Ar and Kr is quite different since now the $B^2\Sigma$ state is more attractive at large R leading to a crossing with the $A^2\Pi$ state at some intermediate distance. This causes a transfer to the lower adiabatic state prior to the region of the asymptotic coupling. In this case $p_{1/2}$ is typically well above the sudden limit of $1/3$ which is approached at higher collision energies from above.

The molecular NaN_2 system shows the aspects of both situations depending on the molecular orientation θ during the collision. The potentials for a collinear arrangement are similar to the case of Na interacting with the lighter rare gases (Fig. 5). Comparable to the situation encountered for the heavier rare gases, a crossing of the σ - and π -type configurations occurs for the T-shaped geometry (Fig. 6). This is also the cause for the occurrence of a conical intersection of the potentials in A' symmetry at $\theta=90^\circ$.

The effect of the molecular orientation is most clearly seen from calculations in which the Na– N_2 angle θ is kept fixed along a trajectory. Figures 7 and 8 show the strong dependence of $p_{1/2}$ on θ with a pronounced maximum at 90° . The sudden limit is only partially reached even at the largest

FIG. 8. Gaussian average of the angular dependence of the nonadiabatic transition probability as in Fig. 7. The numbers in the figure indicate the collision energy in cm^{-1} . The broadening of the distribution with increasing collision energy and the trend to the sudden limit $p_{1/2}=1/3$ is clearly seen.

energies investigated here. In first approximation the observed value of $p_{1/2}$ is an orientational average. Using an angular weight function $\sin\theta$ and the data for fixed θ the value $\bar{p}_{1/2} = \int_0^\pi p_{1/2}(\theta) \sin\theta d\theta$ almost perfectly reproduces the experimental and theoretical findings according to which $p_{1/2}$ is close to $1/3$ for all energies. The latter result is thus not a consequence of the sudden limit which is reached only at much higher collision energies but rather arises from the molecular orientation average and the complementary situations for collinear and T-shaped geometries. More directly, the strong dependence of $p_{1/2}$ on the molecular orientation is also seen from the fact that different initial conditions produce a very broad distribution with $p_{1/2}$ ranging between 0 and ~ 0.8 (Fig. 9). Though the final dependence of $p_{1/2}$ on energy may seem rather unspectacular, it is, however, a direct manifestation of the conical intersection occurring in NaN_2 . In reality the system, of course, evolves under the action of angular dependent forces and the N_2 molecules have initial rotational energy. The initial rotation produces a more or less rapid change of the molecular orientation during the collision and causes an increased averaging. In fact the rotational temperature T_{rot} of the molecule seems to have a small effect on $p_{1/2}$. This is observed in our calculations at

FIG. 9. Distribution of nonadiabatic transition probabilities for a trajectory ensemble with random initial conditions ($\epsilon = 650\text{ cm}^{-1}$, $\Delta = 240\text{ cm}^{-1}$).

very low values of T_{rot} (10 K) and is absent for 100 K and above (Fig. 2). It indicates that a molecule without substantial rotation has a slightly higher chance for the energetically preferred T-shaped geometry of the σ -like state in the coupling region. A preliminary experimental confirmation comes from our earlier experiments using a supersonic target beam. The molecules are expected to have a low rotational temperature in this case, and we actually found $p_{1/2}$ values as large as 0.4.

For the case of negative detuning the collisional complex is initially excited in either the $1^2A'$ or $2^2A''$ states. A slight but significant increase of $p_{1/2}$ is seen for low energies in the red-wing experiment and in the calculation (Fig. 2). In this case smaller final collision energies can be realized compared to the case of positive detuning and the behavior of $p_{1/2}$ for $\epsilon_f \sim 0$ becomes accessible. Under the conditions of the experiment the $1^2A'$ and $2^2A''$ states are initially excited with almost the same probability. For low values of the (final) kinetic energy an adiabatic limit $p_{1/2}$ near 1/2 should be approached. This is in fact seen in Fig. 2. Under the same conditions red- and blue-wing transition probabilities are related by $p_{1/2}^b = (1 - p_{1/2}^r)/2$ given that the final kinetic energies are the same, e.g., $p_{1/2}^r = 0.4$ corresponds to $p_{1/2}^b = 0.3$. This is consistent with the trend to lower $p_{1/2}$ seen in the blue-wing data of Fig. 3.

V. CONCLUSIONS

We have obtained experimental results on the fine-structure branching for the atom-molecule system $\text{Na} + \text{N}_2$. The relative population $p_{1/2}$ is directly related to the nonadiabatic transition probability characteristic for a single passage through the coupling region. In contrast to the case of rare-gas perturbers, $p_{1/2}$ shows little variation with the collision energy and has typical values around 1/3. The analysis performed here by the classical-path method reveals, how-

ever, the profound effect of the conical intersection occurring in NaN_2 for the T-shaped geometry. It induces a strong dependence of $p_{1/2}$ on the $\text{Na}-\text{N}_2$ angle during the collision. The broad distribution of $p_{1/2}$ arising for different initial conditions of the trajectories explains the overall observed values near 1/3. There is, however, a clear trend to the adiabatic limit in the red-wing data. The blue-wing data indicate an effect of the rotational temperature on the branching ratio. Our classical-path calculations with the new diabatic potentials by Spelsberg *et al.*⁸ give a very good agreement between experiment and theory, indicating a very reliable representation of the electronic potentials and of the conical intersection.

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