Experimental Proof of a $|\Delta m| \ll j$ Propensity Rule in Rotationally Inelastic Differential Scattering

A. Mattheus, A. Fischer, G. Ziegler, E. Gottwald, and K. Bergmann[a]

Fachbereich Physik der Universität Kaiserslautern, 675 Kaiserslautern, Federal Republic of Germany

(Received 10 October 1985)

We report the first measurement of a fully state-selected $(v_i, j_i, |m_i|) \rightarrow (v_f, j_f, |m_f|)$ differential cross section in atom-molecule collisions. We have studied Na_2-Ne, $(0,6,|m_i|) \rightarrow (0,0,0)$ rotationally inelastic scattering at a collision energy of 190 meV. The data verify a pronounced $|\Delta m| \ll j$ propensity with respect to the direction of linear momentum transfer. A realistic estimate for the relative contribution of collision processes with $|\Delta m| > 0$ gives an upper limit of 10%.

PACS number: 34.50.Ez

Significant progress has been achieved in recent years in our understanding of the detailed dynamics of such elementary molecular processes as rotationally and vibrationally inelastic collisions.[1-4] Despite this advance, experimental information about collisional reorientation is limited to data almost exclusively from experiments in the bulk that suffer from extensive averaging over scattering angles and directions of relative velocity.

On the experimental side, advances in inelastic scattering were made possible by the development of new techniques for state-selective scattering experiments in crossed molecular beams with[1,2] and without lasers.[3] On the theoretical side, the development of the infinite-order sudden (IOS) approximation[5] had a major impact. The IOS approximation results in a decoupling of the multichannel problem, basically by virtue of the neglect of kinetic-energy change and orbital angular momentum.

Excellent agreement between calculated and measured differential cross sections has been obtained.[1,6] So far, however, such comparisons have been made exclusively for cross sections that are sums over all orientations of the molecular angular momenta. There are two reasons for this. Firstly, experimental data on differential scattering of m-selected molecules were not available, with only two exceptions.[7] Tsou, Auerbach, and Wharton studied scattering of polarized LiF on Ar, without final-state selection. Treffers and Korving determined the second moment of the population distribution over m levels of scattered Na_2 molecules without initial-state selection. Secondly, the results of the IOS scattering calculations are ambiguous as far as the collisional reorientation of the molecular angular momentum is concerned.[8] It has been proposed, however, that the so-called kinematic apse, the axis parallel to the direction of linear momentum transfer $\Delta\hat{\mathbf{k}}$, is the relevant quantization axis along which the selection rule $\Delta m = 0$ or propensity rule $|\Delta m| \ll j$ should hold.[9] In fact, it is easy to show, from angular momentum conservation, that $\Delta\mathbf{j} = \mathbf{R} \times \Delta\mathbf{k}$ is valid.[10,11] Here $\mathbf{R}$ is the vector from the center of the molecule to the point of contact. Obviously $\Delta\mathbf{j}$ is perpendicular to $\Delta\mathbf{k}$ and we thus have $\Delta m = 0$. The question arises: To what extent is this selection rule obeyed in a real system involving repulsive interaction?

Although several techniques for the extraction of information about nonisotropically distributed molecular angular momenta have been described and successfully applied,[10] none of the related experiments can prove the conjectures concerning Δm selection rules. The most detailed work, reported by McCaffery and coworkers,[12] deals mainly with inelastic collisions. Their data provide information about the first few moments of the population distribution over m levels, consistent with a $\Delta m = 0$ selection rule with respect to a laboratory axis. The sensitivity of the data to small changes in

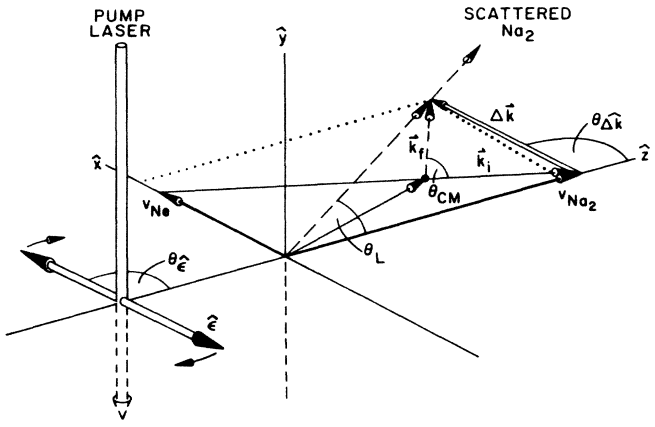

FIG. 1. Schematic experimental arrangement. The flux of scattered molecules in the level $j_f = 0$ is observed at the rotational rainbow angle for the $\Delta j = 6$ transition as $\theta_{\hat{\epsilon}}$ changes. Momentum transfer is along $\Delta\hat{\mathbf{k}}$, which forms an angle of 67° with the molecular beam axis.

m has not been analyzed. It is not expected to be very high. The data of the present experiment are not limited to the first one or two moments of the distribution function over m levels. A sensitivity analysis is straightforward as well. The data provide the first direct and unambiguous proof of the $|\Delta m| \ll j$ propensity rule along $\Delta\hat{\mathbf{k}}$ for Na_2-Ne scattering at a collision energy of 190 meV. In doing so, this experiment puts a common assumption in the theoretical treatment of these processes on a solid base.

An ensemble of molecules with a high degree of alignment along a quantization axis in the scattering plane is labeled by saturated optical pumping with a laser of linear polarization $\hat{\epsilon}$, to the extent that the scattering contribution of molecules in either the $|m| = j$ or $m = 0$ levels can be isolated from the $j_i \rightarrow j_f = 0$ differential cross section. Here, m is defined with respect to the quantization axis $\hat{\epsilon}$. For a given scattering angle θ^L we can identify the direction of the momentum transfer vector $\Delta\hat{\mathbf{k}}$ (see Fig. 1). The observed signal $I(j_i \rightarrow j_f|\theta^L)$ for scattering of molecules out of level j_i into $j_f = 0$ at the angle θ^L should vary as[1]

$$I(j \rightarrow 0|\theta^L) = K \sum_{m'} [n(j,m')_{\text{off}} - n(j,j')_{\text{on}}] \sigma(j,m' \rightarrow 0,0|\theta^L),$$

with the pump laser off and on, where m' refers to the axis $\Delta\hat{\mathbf{k}}$. The constant K includes all quantities that remain constant as $\Delta\theta$ changes. The populations $n(j,m')_{\text{off}} = n(j,j'|\theta_{\Delta\hat{\mathbf{k}}})$ and $n(j,m')_{\text{on}} = n(j,m'|\Delta\theta)$ are related to the population of the levels m'' with respect to the beam axis $\hat{\mathbf{z}}$ and levels m with respect to the laser polarization $\hat{\epsilon}$ by

$$n(j,m'|\theta_{\Delta\hat{\mathbf{k}}}) = \sum_{m''} n(j,m'') |d^j_{m'm''}(\theta_{\Delta k})|^2$$

and

$$n(j,m'|\Delta\theta) = \sum_m n(j,m) |d_{m'm}(\Delta\theta)|^2,$$

respectively. The angle between $\hat{\epsilon}$ and $\Delta\hat{\mathbf{k}}$ is $\Delta\theta = \theta_{\hat{\epsilon}} - \theta_{\Delta\hat{\mathbf{k}}}$ where $\theta_{\hat{\epsilon}}$ and $\theta_{\Delta\hat{\mathbf{k}}}$ are measured relative to the molecular beam axis. The $d^j_{m'm}(\Delta\theta)$ are the rotation-matrix elements.[11] If the selection rule $\Delta m' = 0$ is obeyed with respect to $\Delta\hat{\mathbf{k}}$, the scattering signal $I(j \rightarrow 0|\theta^L)$ should be proportional to $n(j,m' = 0|\Delta\theta)$, because the final state is restricted to $(j_f = 0,\ m_f = 0)$.

The experimental realization of the angular momentum alignment will be discussed in detail in a separate publication.[13] Briefly, we transport laser light to the molecular beam apparatus via a polarization-preserving single-mode fiber. Rotation of the polarization vector $\hat{\epsilon}$ is accomplished by rotation of a $\lambda/2$-plate followed by a high-quality Glan-Thompson polarizer (extinction ratio 10^5:1) that rotates at twice the speed. The latter two components are located inside the vacuum.

Optical pumping in the regime of saturation allows us to deplete the population of all levels with a nonvanishing transition probability. As an example the population of all levels $|m| < 6$ is depleted when a P transition ($j'' = 6 \rightarrow j' = 5$) in the $A \leftarrow X$ band is used but the population of $|m| = 6$ is left unchanged. Use of a Q transition ($j'' = 6 \rightarrow j' = 6$) in the $B \leftarrow X$ band depletes the populations of all m levels except $m = 0$, while saturated pumping on an R transition ($j'' = 6 \rightarrow j' = 7$) depletes the population of all m levels.

The scattering signal $I(j \rightarrow 0|\theta^L)$ is related to the subgroup of the modulated level. It is obtained from the difference of the signals with the pump laser off, I^{off} (all thermally populated levels contribute), and the pump laser on, I^{on} (contribution from the pumped levels is missing).[1] The orientational dependence of the cross section is probed by monitoring the difference of the number of scattered particles with R and P or R and Q pumping as $\hat{\epsilon}$ rotates. The desired experimental information is retrieved by comparison of appropriately normalized scattering data.

Pumping on an R transition we have $n(j,m')_{\text{on}} = 0$ for all m' levels and the scattering signal is given by

$$I^R(j \rightarrow 0|\theta^L) = K \sum_{m'} n(j,m')_{\text{off}} \sigma(j,m' \rightarrow 0,0|\theta^L). \quad (1)$$

For $n(j,m')_{\text{off}} = \text{const}$, this reduces to the result for the m-averaged cross section.[1] Here, we write the cross section as a product of the m-averaged cross section and a function containing the m dependence,

$$\sigma(j,m' \rightarrow 0,0|\theta^L) = \sigma(j \rightarrow 0|\theta^L) g(j,m' \rightarrow 0,0|\theta^L),$$

with the normalization $\sum_{m'} g(j,m' \rightarrow 0,0|\theta^L) = 1$. Equation (1) may then be written in the form

$$I^R(j \rightarrow 0|\theta^L) = K n(j) \sigma(j \rightarrow 0|\theta^L) M^R \quad (2)$$

with $n(j) = \sum_{m'} n(j,m')$ and

$$M^R = n(j)^{-1} \sum_{m'} N(j,m'|\theta_{\Delta\hat{\mathbf{k}}}) g(j,m' \rightarrow 0,0|\theta^L). \quad (3)$$

Pumping on a P transition yields a signal

$$I^P(j \rightarrow 0|\theta^L) = K n(j) \sigma(j \rightarrow 0|\theta^L) M^P \quad (4)$$

with

$$M^P = M^R - 2\frac{n(j,m=j)}{n(j)}\sum_{m'}|d^j_{m'j}(\Delta\theta)|^2 g(j,m'\rightarrow 0,0|\theta^L). \quad (5)$$

Equation (5) implies that pumping on a P transition eliminates the population of all m_j levels *except* $|m|=j$. For Q pumping the term $2n(j,m=j)$ in Eq. (5) must be replaced by $n(j,m=0)$.

The normalized difference $S^P(\Delta\theta)=(I^R-I^P)/I^R$ of the scattering signals for R and P pumping is

$$S^P(\Delta\theta)=\frac{2\sum_{m'}|d^j_{m'j}(\Delta\theta)|^2 g(j,m'\rightarrow 0,0|\theta^L)}{\sum_{m'} g(j,m'\rightarrow 0,0|\theta^L)}. \quad (6)$$

For Q pumping $[S^Q(\Delta\theta)=(I^R-I^Q)/I^R]$ the factor $2|d^j_{m'j}(\Delta\theta)|^2$ must be replaced by $|d^j_{m'0}(\Delta\theta)|^2$. Assumption of $\Delta m'=0$ with respect to $\Delta\hat{\mathbf{k}}$ requires $g(j,m'\rightarrow 0,0|\theta^L)=\delta_{m',0}$ and Eq. (6) reduces to $S^P(\Delta\theta)=2|d^j_{0j}(\Delta\theta)|^2$ or $S^Q(\Delta\theta)=|d^j_{00}(\Delta\theta)|^2$.

Figure 2 shows three experimental curves for P, Q, and R pumping of the level $j_i=6$. The primary beam emerges through a 0.5-mm nozzle from a stagnation pressure of 50 Torr. Scattering events are monitored at the rotational rainbow angle for the $\Delta j=6$ transition[1] by monitoring of the flux of molecules in the level $j_f=0$ as the direction of the linear laser polarization $\hat{\boldsymbol{\epsilon}}$ rotates. As expected, R pumping leads to a constant scattering rate because the population of all m levels is depleted independent of the angle $\theta_{\hat{\boldsymbol{\epsilon}}}$. The fraction of the population of the level $m'=0$ that is not depleted by Q or P pumping reaches its maximum at $\Delta\theta=\theta_{\hat{\boldsymbol{\epsilon}}}-\theta_{\Delta\hat{\mathbf{k}}}=0$ or $\pi/2$, respectively. In fact, the minimum scattering rates are observed at $67^\circ\pm 2^\circ$ and $157^\circ\pm 2^\circ$, respectively, in agreement with expectation.

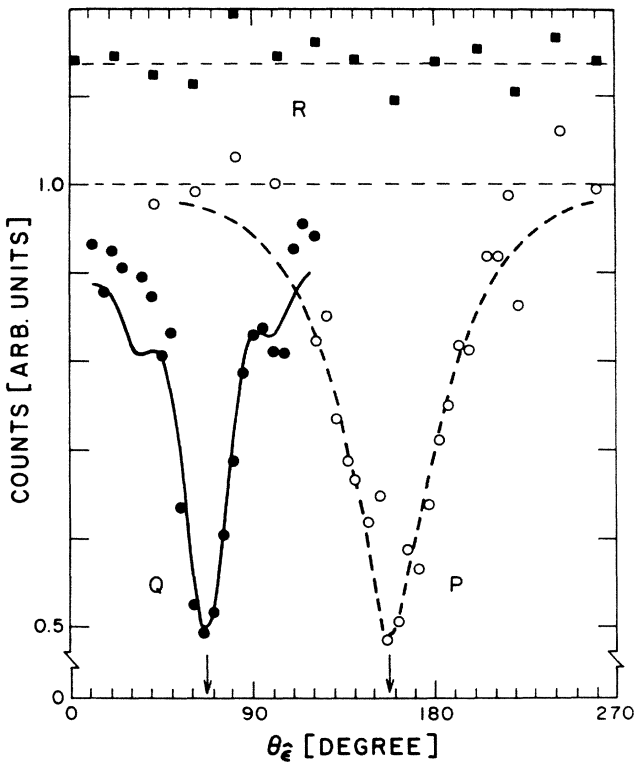

FIG. 2. Variation of the scattering rates I^R, I^P, and I^Q with the angle $\theta_{\hat{\epsilon}}$. I^R, the mean value of which is unity, has been shifted vertically. The arrows mark the angular positions where $\hat{\boldsymbol{\epsilon}}$ is parallel or perpendicular to $\Delta\hat{\mathbf{k}}$. The dashed lines only serve to guide the eye. The solid line is calculated with the assumption of a $\Delta m=0$ selection rule and with hyperfine mixing as well as flow-induced alignment taken into account.

The angular width over which the scattering rate decreases differs by more than a factor of 2 for P and Q pumping for the following reason. On the one hand P pumping leaves the population of molecules in the level $|m|=j$ undepleted. The population in these levels transforms for $\hat{\boldsymbol{\epsilon}}\perp\Delta\hat{\mathbf{k}}$ into the level $m'=0$ as well as levels $|m'|>0$, and the $m'=0$ population reaches only 50% of the population present with no laser pumping. Q pumping, on the other hand, leaves the population of molecules in the level $m=0$ undepleted. This implies that the population of $m'=0$ is expected to reach 100% of the thermal population for $\hat{\boldsymbol{\epsilon}}\parallel\Delta\hat{\mathbf{k}}$. Thus, assuming a $\Delta m'=0$ selection rule in the collisional process, we expect a normalized minimum signal of 0.5 for P pumping, in agreement with the experiment. The minimum signal should be zero for Q pumping, in contrast to the experiment.

Hyperfine precession due to the Na nuclear spin of $I=\frac{3}{2}$ causes mixing of neighboring m levels. The P-pumping data are less sensitive to the effect of hyperfine mixing because more than one m' level remains populated as the angle between $\hat{\boldsymbol{\epsilon}}$ and $\Delta\hat{\mathbf{k}}$ approaches $\pi/2$. By the same token, however, they are less sensitive to small Δm changes in the collision process. A thorough analysis, including the sensitivity of these data to processes with $|\Delta m|>0$ as well as including data of similar quality for $\Delta j=10$, has not been completed at the present time; the dashed line serves only to guide the eye. These experimental results are consistent with a $\Delta m'=0$ selection rule. The Q-pumping data, and in particular the scattering rate at the minimum, are very sensitive to both the effect of hyperfine mixing and collisional reorientation. A rigorous upper limit for the relative contribution of collisions with $|\Delta m'|>0$ can be derived from the fol-

lowing argument. The normalized signal at the minimum ($\hat{\epsilon} \| \Delta\hat{\mathbf{k}}$) is given by

$$S^Q(0) = \frac{g(6,0 \rightarrow 0,0|\theta^L)}{\sum_{m'} g(6,m' \rightarrow 0,0|\theta^L)}$$

[see Eq. (6)]. From Fig. 2 we find $S^Q(0) = 0.5$. Neglect of hyperfine mixing results in a rigorous upper limit on the collisions leading to $\Delta m > 0$ of 50%. Assuming complete hyperfine mixing, however, one finds $S^Q(0) = 0.4$ which is even smaller than observed experimentally. From the distance between the pump region and scattering center, the molecular flow velocity, the width of the velocity distribution, and the known hyperfine splitting,[14] we estimate the mixing to be about 95% complete. The solid line of Fig. 2 has been calculated with use of this number and with only $\Delta m = 0$ processes taken into account. The flow-induced molecular alignment upstream of the pump laser is also included in the calculation and causes the asymmetry of the solid line. The agreement with the experimental curve is excellent in both angular width and magnitude. Therefore, it is a more realistic estimate to assume that less than 10% of the collisions lead to $|\Delta m| > 0$. This upper limit is likely to be further reduced in a future, more complete, sensitivity analysis.

In summary, these experiments provide data for angularly resolved rotationally inelastic scattering in atom-molecule collisions of unprecedented detail. The characterization of the collision process is, however, not yet complete because the initial angular momentum $\mathbf{j}_i$ is restricted to the scattering plane. Nevertheless, this paper presents the first *direct* experimental verification of a pronounced propensity for m preservation with respect to the direction $\Delta\hat{\mathbf{k}}$ of momentum transfer in rotationally inelastic scattering. This result is expected to hold for other collision systems with predominantly repulsive interaction. For less repulsive interactions, and in particular for collisions involving open-shell molecules,[15] this propensity is expected to be weakened.

The technique applied here exploits the full potential of laser state selection. Besides its application to the present problem, it will be relevant for the study of other collision processes where orientational dependence is of interest, such as chemical reactions and molecule surface collisions.

This work has been supported by the Deutsche Forschungsgemeinschaft under Sonderforschungsbereich 91. We thank U. Hefter for significant contributions to the experimental implementation and analysis of the m-selection scheme used in this experiment. One of us (K.B.) is grateful for a Joint Institute for Laboratory Astrophysics (University of Colorado and National Bureau of Standards, Boulder) Visiting Fellowship that helped to complete this work.

[a]1985 Visiting Fellow, Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colo. 80309.

[1]P. L. Jones, U. Hefter, A. Mattheus, K. Bergmann, W. Müller, W. Meyer, and R. Schinke, Phys. Rev. A **26**, 1283 (1982).

[2]W. P. Moskowitz, B. Stewart, R. M. Bilotta, J. L. Kinsey, and D. E. Pritchard, J. Chem. Phys. **80**, 5496 (1984).

[3]M. Faubel, Adv. Atom. Mol. Phys. **19**, 345 (1983).

[4]G. Hall, K. Liu, M. J. McAuliffe, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **81**, 5577 (1984); E. Gottwald, A. Mattheus, K. Bergmann, and R. Schinke, J. Chem. Phys., in press.

[5]G. A Parker and R. T. Pack, J. Chem. Phys. **68**, 1585 (1978).

[6]R. Schinke and J. M. Bowman, in *Molecular Collision Theory,* edited by J. M. Bowman (Springer, Heidelberg, 1983), Chap. 4.

[7]L. Y. Tsou, D. J. Auerbach, and L. Wharton, Phys. Rev. Lett. **38**, 20 (1977), and J. Chem. Phys. **70**, 5296 (1979); M. A. Treffers and J. Korving, Chem. Phys. Lett. **97**, 342 (1983).

[8]R. Schinke and H. J. Korsch, Chem. Phys. Lett. **74**, 449 (1980).

[9]V. Khare, D. J. Kouri, and D. K. Hoffmann, J. Chem. Phys. **79**, 4493 (1982).

[10]M. P. Sinha, C. D. Caldwell, and R. N. Zare, J. Chem. Phys. **65**, 491 (1974); A. G. Visser, J. P. Bee Koy, L. K. van der Meij, C. de Vreugd, and J. Korving, Chem. Phys. **20**, 391 (1977).

[11]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton Univ. Press, Princeton, N.J., 1957).

[12]S. R. Jeyes, A. J. McCaffery, M. D. Rowe, and H. Kato, Chem. Phys. Lett. **48**, 91 (1977).

[13]U. Hefter, G. Ziegler, A. Mattheus, A. Fischer, and K. Bergmann, to be published.

[14]S. D. Rosner, R. A. Holt, and T. D. Gaily, Phys. Rev. Lett. **35**, 785 (1975).

[15]T. Orlowski and M. H. Alexander, J. Chem. Phys. **80**, 4133 (1984).