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Resolution of interference effects in the rotational excitation of NO (N=O) by Ar

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In a state-to-state experiment integral cross sections for the rotational excitation of NO ($N=0$) by Ar have been measured in a cross beam experiment with two pulsed nozzle sources by analyzing the rotational distribution of NO by LIF. For the first time an odd–even interference structure in the final rotational distribution is clearly resolved. Coupled states calculations using an electron gas model potential reproduce qualitatively the experimentally observed structure.

In the last few years a much deeper insight into the dynamics of rotational excitation was achieved by use of modern experimental methods in molecular beam experiments. [1,2] Initial state preparation by rotational cooling in nozzle beams and state selective detection methods like LIF enabled the experimentalist to do state-to-state experiments. A series of experiments concentrated on the measurement of differential cross sections using TOF as well as LIF as detection methods. [3] A few experiments were done with state selected molecules for integral state-to-state cross sections for rotational excitation. [4] A main difference to these experiments is that we are using pulsed molecular beam sources and a pulsed UV probe laser. The anisotropy in the NO–rare gas systems was formerly studied by Thuis *et al.* analyzing the orientational dependence of the glory structure of total cross sections. [5] Here we probe the anisotropy in a more direct way and determine $0 \rightarrow N'$ integral cross sections at a fixed collision energy.

The experimental setup consists essentially of two identical pulsed molecular beam sources mounted at right angle. These sources, originally designed by Liverman *et al.*, [6] have an open time of ~ 100 μs, nozzle holes of 600 μ ϕ and work at a repetition rate of 5 Hz. Two skimmers located 4.5 cm downstream with a ϕ of 1.25 mm define the size of the scattering center that is 14 cm downstream. The NO beam is seeded in Ar (5%, $p_0 \sim 1.5$ bar) and we obtain a rotational temperature of ~ 2 K corresponding to a ratio of $1:10$ for the NO ($N=1$) relative to NO ($N=0$) population. The secondary beam is a pure Ar beam ($p_0 \sim 4.5$ bar). The rotational distribution of NO is measured by LIF, directly irradiating the scat-

tering zone with a tunable UV laser at 226 nm exciting the $^2\Pi-^2\Sigma$ transition of NO. The tunable UV is obtained by mixing the 1.064 nm of a Nd:YAG with the frequency doubled output of the Nd:YAG pumped dye laser. The fluorescence is measured by a phototube; filters and baffles are used to suppress scattered light. To increase S/N, a boxcar integrator is used and we average ~ 3 min corresponding to 1000 gas pulses. The difference signal with and without secondary beam divided by Hönl London factors gives the relative populations in the rotational states. The timing is synchronized by a central clock that triggers the probe laser and both pulsed sources with variable delays. An important point is that the laser probes the NO distribution to a time where both gas pulses overlap each other right in the middle, because at the beginning and the end of a pulsed beam the cooling is not as good as stated above. [7]

The resulting density of the $0 \rightarrow N'$ transitions is plotted vs N' in Fig. 1. Except for the oscillations the distribution declines monotonically from its maximum value at $N' = 2$. Remarkable is the relatively large magnitude of the cross sections for the highest transitions just below the limit determined by energy conservation, i.e., $N' = 15$, indicating a strong coupling between the rotational and the translational motion. Two oscillations with minima at $N' = 3$ and $N' = 5$ are clearly resolved and demonstrate the preference of even vs odd N' transitions. However, this propensity is suspended at larger transitions, $N' \gtrsim 7$, and a tendency to preferably populate odd states (inverse-propensity) is slightly indicated by the two shoulders at $N' = 9$ and $N' = 13$.

This oscillating structure is believed to stem primarily from the asymmetry of the heteronuclear NO molecule. This surmise is substantiated by coupled-states [8] calculations using the electron gas potential energy surface V_a of Nielson *et al.* [9] and treating NO as a Σ molecule. The results are also shown in Fig. 1. Qualitatively similar results were obtained with the MS potential from Ref. 5 but not indicated here. In order to compare with the experimentally determined *densities*, we calculate here theoretical densities by averaging the
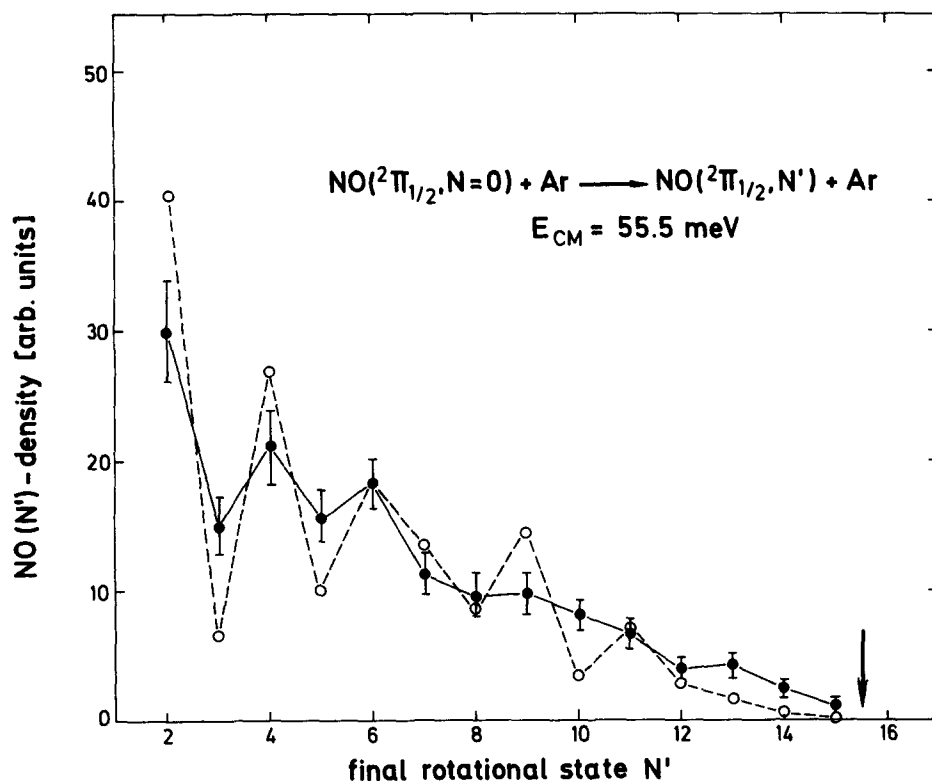
FIG. 1. NO(N') density for rotational of NO($^2\Pi_{1/2}$, $N = 0$) in collisions with Ar. Solid lines: experiment; broken line: theory. Error bars are standard deviations by various measurements. The theoretical distribution is normalized to the experimental one at $N' = 6$. Data are obtained via the R_1, R_1, and Q_1 branch. The arrow indicates the energy limit.

calculated differential cross sections. This corresponds to the usual flux-density transformation done in reactive experiments.[10] Although the comparison with the experimental cross sections is only fair, the qualitative behavior especially the odd – even oscillations between $N' = 1$ and $N' = 7$, is correctly reproduced. The preference of odd N' transitions for $N' > 7$ is clearly visible. Using classical S matrix theory, McCurdy and Miller[11] interpreted these structures as a interference effect between scattering from the two different ends of a heteronuclear molecule. It cannot be properly described by a complete classical theory which does not include interference.[12] An analog interpretation follows also from the semiclassical limit of the infinite-order sudden approximation.[13]

As anticipated by McCurdy and Miller[11] these "interference structures are an extremely sensitive measure of anisotrophy in the interaction potential." In accordance with their model calculations we find by varying the original electron gas potential surface that the oscillations are damped if the ratio V_1/V_2 is increased with V_λ being the λth coefficient in the usual Legendre polynominal expansion. An accurate determination of the NO–Ar potential surface will be attempted in the future when a more extended set of experimental data covering a wider range of collision energies is available.

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