curves because of the difficulty of exactly replicating, during the measurement of the pure oxygen data, the conditions under which the ozone data were taken. Slight differences in resolution and incident energy, and the variation of incident current with energy, cause some "leakage" of oxygen vibrational structure into the reduced curves. When all of our data sets are taken into consideration, this substructure can be seen to be an artifact.

These results can be compared with those of Hay, Dunning, and Goddard.[5] Figure 2 shows their calculated vertical excitation energies to the $^3B_2$, $^3A_2$, $^1A_2$, and $^3B_1$ states. The lowest excited state, the $^3B_2$ state, has a calculated adiabatic transition energy of 0.7 eV and a vertical transition energy of 1.47 eV. The difference between the calculated adiabatic and vertical energies is expected to be more accurate than either separately, with both subject to the same systematic offset. Since the dissociation energy is 1.13 eV, the $^3B_2$ state would be stable against dissociation if its vertical transition energy lies below 1.9 eV. The observed structure is approximately what would be expected from the sum of four broad peaks. In particular, even under the most extreme assumptions, given the shapes of the calculated energy surfaces, the intensity maximum near or below 1.7 eV shows that one or more of the states calculated are almost certainly stable against dissociation. This stability opens another channel in the normal three-body reaction for ozone formation, with the end product being a more highly reactive species of ozone. This state will now require consideration in kinetics experiments and, depending on its lifetime, in atmospheric modeling as well.

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Measurement of the Zero-Field Hyperfine Structure of a Single Vibration-Rotation Level of Na_2 by a Laser-Fluorescence Molecular-Beam-Resonance Technique*

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By replacing the *A* and *B* magnets of the conventional molecular-beam-resonance technique with laser optical-pumping regions, we have developed a method for the observation of hfs in a single molecular-vibration-rotation level of arbitrary *J*. We obtain for the electric quadrupole and spin-rotation constants of the $X\,^1\Sigma_g^+, v''=0, J''=28$ level of Na_2: $eqQ = -463.7 \pm 0.9$ kHz; $|c| = 0.17 \pm 0.03$ kHz. We also report the first observation of a spin-rotation transition.

Much of our knowledge of the properties of free atoms and molecules has come from the molecular-beam-resonance technique developed principally by Ramsey and co-workers.[1] This method is well suited to high-precision measurements of hyperfine structure in low rotational levels of neutral molecules. In an electric-deflection beam spectrometer, rotational levels of polar molecules with $J \lesssim 5$ may be individually studied because of the sizable J dependence of their deflection properties in the inhomogeneous electric field.[2] In a magnetic-deflection apparatus, homonuclear diatomic molecules can be studied, but, except for the lightest molecules like H_2 or molecules from a low-temperature source, the spectra obtained represent averages over many thermally populated rotational levels since these levels have essentially J-independent deflection properties. In both the electric and magnetic cases, an observable transition must bring about a change in beam trajectory, and hence it must occur between levels with substantially different effective moments; also the beam itself must be detected, with efficiencies ranging from 100% to less than 0.1%.

Following a suggestion by Kastler, several workers[3,4] have replaced the A and B magnets of the conventional atomic-beam apparatus by optical-pumping regions employing resonance lamps and more recently lasers.[5] In some cases, this technique has been used to do magnetic-resonance studies of atomic ground states.

In the present experiment, we have observed the zero-field hfs of a single vibration-rotation level of Na_2 by magnetic resonance in a molecular beam, using an Ar^+ laser instead of the conventional A and B magnets. This work augments the conventional deflection techniques in two significant ways. First, the observation of only one vibration-rotation level has permitted an unambiguous determination of the electric quadrupole and spin-rotation constants of that level, as opposed to a measurement of averages over all thermally populated levels. Secondly, the ability to observe a single level of high J has made possible the direct observation of a spin-rotation transition, i.e., a transition between two hyperfine levels which would be degenerate in the absence of the spin-rotation interaction.

The apparatus consists of a Na_2 beam source, two regions A and B where the molecular beam is crossed by a linearly polarized laser beam, and an intermediate region C where the magnetic resonance takes place. At the A crossing, molecules in the $v''=0, J''=28$ level of the ${}^1\Sigma_g{}^+$ ground state are excited to the $B\,{}^1\Pi_u, v'=6, J'=27$ level by the 476.5-nm Ar^+ laser line. The relatively intense resulting fluorescence was spectrally analyzed to confirm the identification of the levels. Because of the variation of absorption probability with magnetic quantum number, the Zeeman sublevels of the $v''=0, J''=28$ level will be unequally populated after the molecule has traversed the A crossing. Once a molecule has absorbed a photon, it has a very small probability of returning to the same vibration-rotation level in which it began; thus the beam is optically pumped by depletion of highly absorbing levels.[6] At the B crossing, a second beam from the same laser excites the same vibration-rotation level, and the resulting fluorescence is detected. If an rf field in the C region redistributes the molecules among the various sublevels of the $v''=0$, $J''=28$ level, those sublevels with high absorption probabilities will be repopulated and hence the fluorescence at B will increase. The resonance signal is obtained by chopping the C field and synchronously detecting the change in the B fluorescence.

The Na oven was typically run at 620°C (34 Torr), and produced a supersonic beam whose intensity remained very stable for long periods. The velocity distribution of the beam was measured by a new laser-induced–fluorescence technique involving time of flight.[7] The distribution showed the narrowing and peak shift characteristic of supersonic beams with a Mach number of 4. A lower bound on the beam flux, obtained by assuming 100% efficiency for the detector, is 7×10^{16} particles/sec sr. With 5% for the dimer mole fraction, this translates to 3×10^{11} Na_2 molecules/sec passing through the B crossing region.

The laser was operated at about 0.1 W at 476.5 nm with an intracavity etalon installed to select a single longitudinal mode. The width of the mode was much less than the 90-MHz width (primarily Doppler) of the molecular absorption profile. To maintain a stable fluorescence signal it was necessary to control the cavity length with a servo loop, using a thermally regulated Fabry-Perot interferometer as the reference. The fluorescence intensity at B with the A laser beam blocked was checked at the beginning and end of each 20-sec data-collection period and was found to be constant within ± 3%.

Fluorescence at B, filtered to remove scattered light at 476.5 nm, was detected by a cooled photomultiplier. At a gain of about 10^7, the photocurrent was 7 μA with the A laser beam blocked. Unblocking the A beam typically decreased the B fluorescence by a factor of 10 because of the optical pumping. The photomultiplier pulses were amplified and then scaled by an up-down counter. A flattened solenoid, 36.2 cm long, produced rf magnetic fields of amplitudes up to 20 G, chopped at 107 Hz. The square-wave chopping envelope provided the reference signal for the up-down counter. The theoretical resolution of the apparatus, based on the molecular transit time in the C field, was about 3.6 kHz.

The Na^{23} nucleus has spin $\frac{3}{2}$, so the homonuclear diatomic molecule can have total nuclear spin 0 or 2 in an even J'' level of the ground electronic state. The six hyperfine levels, $F''=26$ to 30, are split by several internal interactions in the molecule, given by the following Hamiltonian[1,2]:

$$\mathcal{H}_{\mathrm{hfs}}=\mathcal{H}_Q+\mathcal{H}_{\mathrm{sr}}+\mathcal{H}_{\mathrm{ss}}+\mathcal{H}_{\mathrm{ss}}'.$$

The most important term is $\mathcal{H}_Q$, which represents the coupling of the nuclear electric quadrupole moments to the molecular electric field gradient. The matrix elements of $\mathcal{H}_Q$ in the $|IJFM_F\rangle$ representation have recently been summarized by Hanes *et al.*[8] An estimate of the quadrupole coupling constant eqQ was obtained by Logan, Coté, and Kusch[9] from nuclear magnetic resonance in a molecular beam. They found[10] $eqQ=-423$ kHz as the average value for all the vibration-rotation levels populated in the beam, by comparing their data with a theoretical line shape calculated on the assumption that $J''\gg 1$ and is a continuous variable.

The spin-rotation interaction, $\mathcal{H}_{\mathrm{sr}}$, represents the magnetic coupling of the nuclear dipole moments to the molecular rotation. Although the magnitude of c, the spin-rotation constant, is very small compared to eqQ, its effect becomes observable in high rotational levels. The terms $\mathcal{H}_{\mathrm{ss}}$ and $\mathcal{H}_{\mathrm{ss}}'$ represent the tensor and scalar parts of the nuclear spin-spin interactions. Reasonable estimates of the coupling constants indicate that the contribution of these interactions to the rf spectrum is well below the precision of the present work.[11]

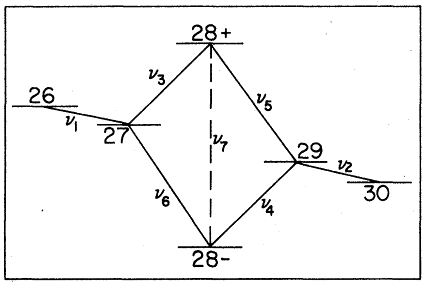

FIG. 1. Schematic hfs of $J''=28$ for $eqQ<0$ and $c>0$. The energy levels (not to scale) are labeled by F'', and the transition frequencies ν_1–ν_7 are given in Eqs. (1).

Diagonalization of $\mathcal{H}_Q+\mathcal{H}_{\mathrm{sr}}$ yields the following expressions for the transition frequencies $\nu(F_1'', F_2'')$ in the $J''=28$ level, neglecting terms of second order in c/eqQ:

$$\begin{aligned}&\nu_1\equiv\nu(26,27)=27c,\quad \nu_2\equiv\nu(29,30)=30c,\\ &\nu_3\equiv\nu(27,28^+)=-0.25eqQ-29.5c,\\ &\nu_4\equiv\nu(28^-,29)=-0.25eqQ-27.5c,\\ &\nu_5\equiv\nu(28^+,29)=-0.25eqQ+27.5c,\\ &\nu_6\equiv\nu(27,28^-)=-0.25eqQ+29.5c,\\ &\nu_7\equiv\nu(28^+,28^-)=-0.50eqQ.\end{aligned}\tag{1}$$

Here, $F''=28^+$ and 28^- refer to the two linear combinations of $F''=28, I=0$ and $F''=28, I=2$ that diagonalize $\mathcal{H}_Q+\mathcal{H}_{\mathrm{sr}}$. Figure 1 shows schematically the hyperfine splitting of $J''=28$ with these seven transitions indicated. The pairs of transitions (ν_1,ν_2), (ν_3,ν_4), and (ν_5,ν_6) are each unresolvable, having a splitting of less than 500 Hz. The $\Delta F''=0$ transition, ν_7, is expected to be very weak.

Figure 2 shows the experimental spectrum at an rf field amplitude of $H_1=7.7$ G. At this field, the up-down accumulation at a resonance peak was typically 10^3 counts/sec on a background flu-

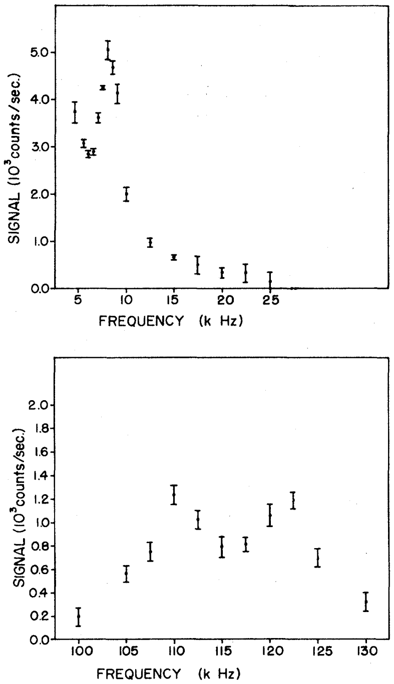

FIG. 2. rf spectrum of $J''=28$ level at $H_1=7.7$ G. Error bars represent observed scatter rather than counting statistics.

orescence of 1.5×10^5 counts/sec. The signal vanished within the noise when the A laser beam was blocked, verifying that the source of polarization in the molecules was indeed optical pumping, and also that spurious effects arising from rf pickup on the B photomultiplier were not present. Investigation of the dependence of the spectrum on H_1 shows that the position of the two high-frequency peaks remains unchanged, while the low-frequency peak exhibits an enormous shift arising from the Bloch-Siegert effect. A recent semiclassical treatment by Pegg[12] of magnetic resonance in a spin-$\frac{1}{2}$ system for arbitrary H_1 reproduces the well-known first-order shift proportional to H_1^2, and predicts a resonance position linear in H_1 in the limit of very large H_1. Although we are far from dealing with a spin-$\frac{1}{2}$ system here, a plot of apparent peak position versus H_1^2 for values of H_1 up to approximately 19 G, shown in Fig. 3, exhibits similar behavior.

Linear extrapolation of the curve of Fig. 3 to $H_1^2=0$, using the three lowest points, yields a value of 4.14 ± 0.07 kHz for the low-frequency peak, where the error is purely statistical. If we identify this value with the mean of ν_1 and ν_2 we obtain $|c|=0.145\pm0.003$ kHz. However, as Cohen-Tannoudji, Dupont-Roc, and Fabre[13] remark, and as is evident in Fig. 2, the distortion of the resonance peak may introduce systematic error into the determination of the center. We view the above value of c as a lower bound.

The two high-frequency peaks provide a value of eqQ and a second, independent value of $|c|$. Since the Bloch-Siegert shift for these transitions is negligible, the counter-rotating component of the rf field can be ignored and the calculation of the line shape for each transition can be done exactly. However, we have neglected the fact that the two pairs (ν_3, ν_4) and (ν_5, ν_6) are not completely resolved, so that a molecule may be driven coherently among the four hyperfine levels $F''=27$, 28^+, 28^-, 29, possibly changing the peak separation (without shifting the mean frequency). The best fit of the summed theoretical line shapes to the high-frequency data of Fig. 2 gives

$$eqQ=-463.7\pm0.9\text{ kHz},\quad |c|=0.201\pm0.006\text{ kHz}.$$

Our best estimate of $|c|$ is the average of the values from the low- and high-frequency data, with an error large enough to include both: $|c|=0.17\pm0.03$ kHz. A more exact treatment of both the high- and low-frequency peaks should yield a more precise value for $|c|$.

The growing sophistication of tunable lasers increases the flexibility of the present method for the study of molecular hfs and rotational moments as a function of v'' and J''. While a reasonably intense light source at the proper frequency is necessary, the absence of beam deflections means that wider beams can be used, and the usual bombardment-ionizer, mass-spectrometer detector replaced by a photomultiplier. The method also offers a real possibility of ion-beam-resonance spectroscopy, and such an experiment is presently underway.

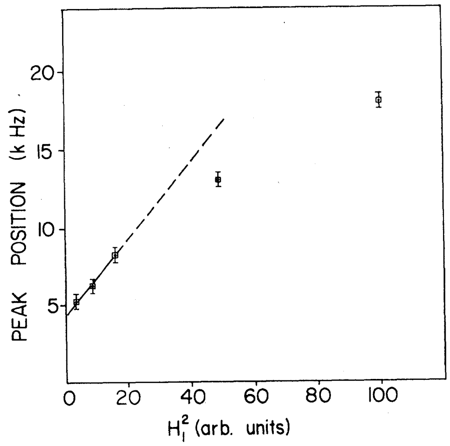

FIG. 3. Position of low-frequency peak as a function of H_1^2. The straight line is the best fit to the lowest three points.

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Direct Computation of Dynamical Response by Molecular Dynamics: The Mobility of a Charged Lennard-Jones Particle

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A nonequilibrium molecular-dynamics method of computing the dynamical response is presented. It is applied to the mobility of a charged particle in a Lennard-Jones liquid and the results agree with those computed from the Green-Kubo formula and with experimental data on argon. A discussion is given of the linearity of the mechanical response. The linear-response term is evaluated explicitly by a perturbation formula and the character of the nonlinear terms is briefly considered.

In this Letter we present a method of computing directly by molecular dynamics (MD) the full dynamical response of a model system of interacting particles to an external disturbance. The method is simply an exploitation of Liouville's theorem and of the possibility offered by MD of computing the perturbed mechanical trajectory in phase space. Let us define in the $6N$-dimensional phase space Γ of our system the complete Hamiltonian, including the perturbation, as

$$H(p,q,t)=H_0(p,q)+H_{\text{ext}}(p,q,t), \tag{1}$$

and let $\alpha(p,q)$ be a dynamical variable on Γ. If $H_{\text{ext}}(p,q,t)=0$ for $t\leqslant 0$, $\rho_e=C\exp[-H_0/k_BT]$ is the equilibrium distribution function of the unperturbed system, and $\rho(p,q,t)$ is the one corresponding to the complete Hamiltonian (1), obtained by solving the Liouville equation with the initial condition $\rho(p,q,0)=\rho_e$, then we can write that $\rho(p,q,t)=S^\dagger(t,0)\rho_e$, where $S^\dagger(t,0)$ is the adjoint of the complete time-evolution operator. In such conditions, as a consequence of the measure invariance of phase space under natural motion, the time-dependent average of the dynamical variable $\alpha(p,q)$ in the perturbed system can be expressed in terms of the equilibrium average of the quantity $\alpha(p(t),q(t))=S(t,0)\alpha(p,q)$. In fact we have in an obvious way

$$\langle\alpha,\rho(t)\rangle=\langle\alpha,S^\dagger(t,0)\rho_e\rangle=\langle S(t,0)\alpha,\rho_e\rangle. \tag{2}$$

By the MD technique we can obtain the nonequilibrium average $\langle\alpha,\rho(t)\rangle$ by starting at $t=0$ from various configurations of the equilibrium trajectory, given by the simple H_0 evolution, and computing the complete H evolution of the system between $t=0$ and $t=t$:

$$\langle\alpha,\rho(t)\rangle=\langle S(t,0)\alpha,\rho_e\rangle$$
$$=\lim_{N\to\infty}N^{-1}\sum_{n=1}^{N}S_0(t_n,0)S(t_n+t,t_n)\alpha, \tag{3}$$

where $S_0(t_n,0)$ is the H_0 time-evolution operator and the times t_n correspond to reasonably uncorrelated subsequent configurations of phase space that the system reaches along its equilibrium path.

The mobility of a charged particle in a Lennard-Jones (LJ) liquid has been determined in this way, taking into account ion-induced dipole interactions but neglecting dipole-dipole terms. We have followed closely the methods used in the MD "experiments" of Verlet and co-workers.[1] The sample used consisted of 256 particles. The pair potential between the neutral particles was taken as the LJ interaction $\Phi_{\text{LJ}}(r_{ij})$, with parameters appropriate to argon ($\sigma=3.405$ Å, $\epsilon/k_B=119.8$ K), and that between the single charged particle and the other 255 as the LJ interaction modified by the charge-induced dipole term:

$$V(r_{ij})=\Phi_{\text{LJ}}(r_{ij})-\tfrac{1}{2}\alpha e^2 r_{ij}^{-4}.$$

For the value of the atomic polarizability α we have assumed 1.6 Å^3. The LJ interaction was truncated at 2.5σ and the electrostatic interaction at 3.3σ.

In implementing the method, the MD runs are