state in Ni might be used conceptually in either localized or band-structure descriptions of the magnetism in Ni. We also remark that if multiplet effects are important in Ni, as shown here, then they should not be ignored in other transition metals like Co and Fe.

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Scattering of Vibrationally Excited NO off LiF and CaF_2 Surfaces

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The scattering of a pulsed supersonic beam of vibrationally excited ($v'=1, J'=\frac{3}{2}$) nitric oxide molecules, prepared by tunable ir laser excitation, off LiF and CaF_2 surfaces has been investigated by resonantly enhanced two-photon ionization. A survivial probability of less than 2.3×10^{-4} has been found. Similarly, an upper limit of less than 2×10^{-3} can be given for an energy transfer into other rotational states of $v'=1$ or high J'' of $v''=0$. The present results will be compared with the predictions of a recent theoretical model calculation.

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Recently there has been much interest in studying the internal energy distribution of molecules scattered from surfaces.[1-8] Energy distribution of the translational,[7] rotational,[1-5] electronic,[6] and vibrational[8] degrees of freedom has been reported. In these experiments the incident molecules were all in the ground vibrational band distributed over several rotational states. Very little, however, is known experimentally for the interesting case of incident molecules that are vibrationally excited, although a theoretical study of this problem has appeared recently.[9] In this Letter we report the first experimental study of the scattering of vibrationally excited ($v'=1$) nitric oxide molecules off a LiF and a CaF_2 surface, with the incident vibrationally excited molecules all prepared in a single rotational state.

The experiments were performed with pulsed (full width at half maximum, 600 μs; nozzle diameter, 0.44 mm) supersonic beams of pure NO and of 10% NO seeded in He at backing pressures of 180 and 450 Torr, respectively. A skimmer (0.62 mm diam) was placed 16 mm downstream to define a collimated molecular beam entering the UHV scattering chamber. The population distribution over the rotational states in this beam is nonequilibrial,[10] but most (95% for the seeded beam) of the population is concentrated in the lowest five to six rotational states of $X^2\Pi_{1/2}$, and their population ratio can be described by a temperature of about 27 and 8.5 K for the pure and the seeded beam, respectively. Nitric oxide molecules were detected state selectively by resonant two-photon ionization via the $(A^2\Sigma^+ \leftarrow X^2\Pi)$ $\gamma(0\text{-}0)$ and $\gamma(1\text{-}1)$ bands. NO^+ ions were detected by a secondary electron multiplier. The tunable uv probe light ($\Delta\tilde{\nu}_{uv} \sim 0.4$ cm^{-1}, $t=4$ ns, $I=10$ μJ/pulse) was generated by frequency doubling of the output of a neodymium-doped yttrium-aluminum-garnet (Nd:YAlG) laser-pumped Coumarin dye laser in a potassium pentaborate (KB5) crystal. The tunable ir light for the production of vibrationally excited molecules has been generated by difference frequency mixing of the output of a dye laser and part of the second harmonic ($\lambda = 532$ nm) of the dye-laser-pumping Nd:YAlG laser in a $LiIO_3$ crystal,[11] yielding a pulse energy of about 5–10 μJ at a bandwidth of $\Delta\tilde{\nu}_{ir} \sim 0.4$ cm^{-1}. Both lasers could be continuously delayed in time against each other. The ir laser beam was slightly focused to a beam waist of ~0.3 mm and intersected the molecular beam at right angles, polarized perpendicular to it. The uv laser beam was also slightly focused ($f=500$ mm) and directed parallel to the ir beam, polarized in the direction of the molecular beam. This beam could be moved precisely to measure either the population in the molecular beam before it hit the surface or the population distribution in the scattered beam under otherwise identical experimental conditions and without opening of the chamber. The ir excitation pulse intersected the pulsed molecular beam 220 μs after the first part of this beam had passed by to ensure homogeneous supersonic flow conditions.

A LiF crystal (25.4 mm diam × 2 mm) was placed 30.5 mm downstream of the intersection of the ir laser and the molecular beam. The incidence angle of the molecular beam onto the surface was 30°. Before each run the crystal was heated in UHV to about 550–600 K for several hours.[12] Measurements were performed with hot and cooled-down surfaces. The diameter of the molecular beam at the surface was ~2 mm and the equivalent NO density about 6×10^{12} cm^{-3} for the seeded NO/He beam. The conditions for the experiments with the CaF_2 surface were the same, except the incidence angle of the molecular beam was 15°.

The rotational energy distribution for ground-state molecules scattered off the LiF surface ($T_s \sim 300$ K) at a nonspecular angle ($\theta_s = -10°$) is shown in Fig. 1, where $N_{J''}/(2J''+1)$ is plotted versus the internal energy. The normal kinetic energy E_n was 1280 cm^{-1}. Clearly two different regions can be distinguished. For J'' larger than $\frac{11}{2}$, the population can be readily described by a Boltzmann distribution with a temperature of 300 K. However, the population in the low J'' states ($<\frac{11}{2}$) counting for 60% of the molecules corresponds to a Boltzmann distribution of much lower temperature, about 33 K. This is quite different from scattering off Ag[3] where a Boltzmann distribution can be fitted to J'' states up to $\frac{41}{2}$ and

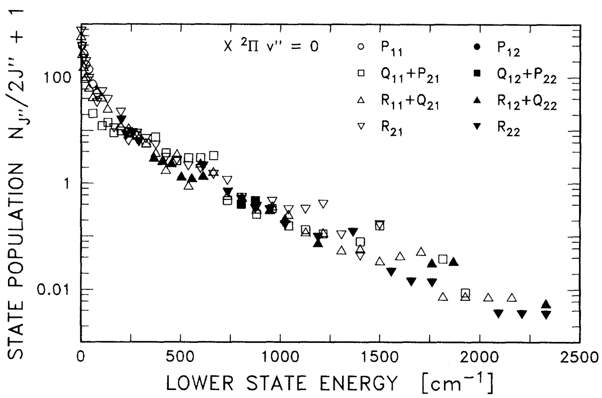

FIG. 1. Rotational state distribution for ground-vibrational-state NO molecules scattered off a LiF surface. The population distribution above ~200 cm^{-1} internal energy can be described by a rotational temperature of $T_{rot} = 300$ K. $E_n = 1280$ cm^{-1}, $\theta_i = 30°$, $\theta_s = -10°$, $T_s = 300$ K.

yield rotational temperatures of at least 300 K. Somewhat surprisingly, in spite of this large quasielastic component, we were also able to detect vibrationally excited molecules off the LiF surface, similar to that in NO/Pt scattering reported recently.[8] The rotational distribution of these vibrationally excited scattered molecules corresponds to a temperature of 49 K, with the total population in $v'=1$ being 4.4×10^{-5} of that in the $v''=0$ population ($T_{\text{vib}}\sim270$ K) for the pure NO beam ($E_n=557$ cm^{-1}).[13]

With the ir laser now tuned to the $R_{11}(J''=\frac{1}{2})$ transition at[14] $\tilde{\nu}=1876.076$ cm^{-1} the incident molecules were vibrationally excited to the single rotational state $X^2\Pi_{1/2}(v'=1, J'=\frac{3}{2})$. Probing the population in the beam via the γ(1-1) band yields the spectrum shown in Fig. 2(a). Only four lines appear, all originating from the single rotational state ($v'=1, J'=\frac{3}{2}$) as expected. Measuring, under the same experimental conditions, the population distribution in $v''=0$ we were able to obtain an absolute calibration of the population in ($v'=1$, $J'=\frac{3}{2}$) which corresponded to 0.6% of the total beam, taking the different Franck-Condon factors for the γ(0-0) and the γ(1-1) band into account.[15] The spectrum in Fig. 2(a) was measured at a spatial separation of 7 mm between the ir and the uv laser beams, resulting in a time delay between both pulses of 6 μs, as shown in Fig. 2(b). From this, the velocity (and hence the kinetic energy) of the NO molecules in the beam could be determined. They were 770 and 1170 m/s for the pure and the seeded beams, respectively, in good agreement with gas dynamic theory.[16]

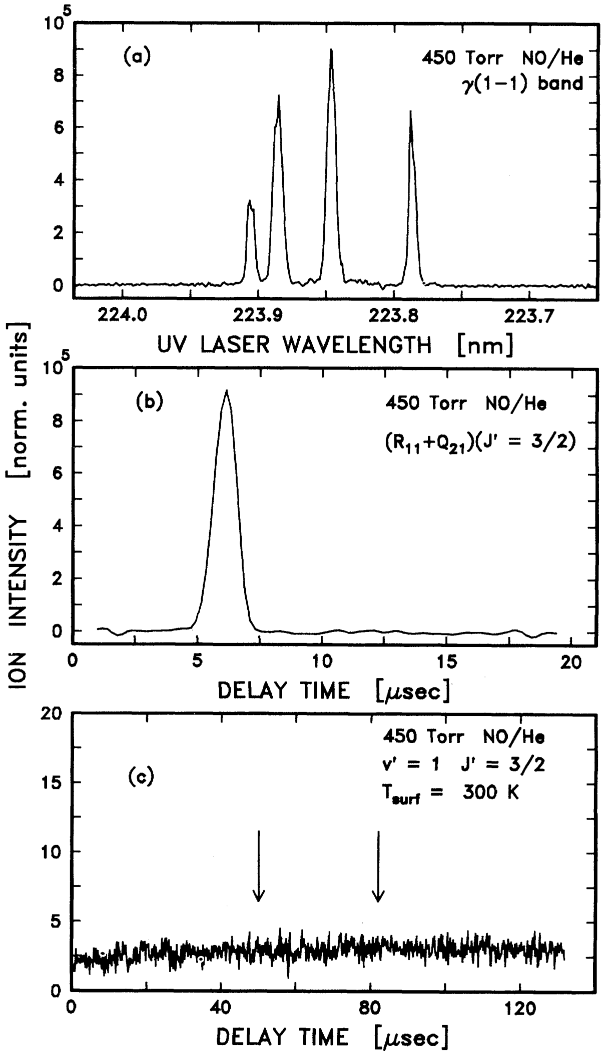

FIG. 2. Ion signals obtained in the ir/uv double resonance (a) as a function of the uv probe-laser wavelength at constant time delay of 6 μ s and (b), (c) as a function of time delay between ir and uv lasers. In (a) the four lines of the P_{11}, $(Q_{11}+P_{21})$, $(R_{11}+Q_{21})$, and R_{21} branches originate all from the same ($v'=1, J'=\frac{3}{2}$) rotational state. In (b) the uv laser is tuned to the $(R_{11}+Q_{21})(J'=\frac{3}{2})$ transition while changing the time delay between the ir and uv lasers before the molecules hit the surface. The time delay spectrum in (c) is obtained under conditions identical to (b) except that now molecules scattered off the LiF surface are probed. Note the greatly enhanced scale in (c).

After scattering the vibrationally excited molecules off the surface, we probed the population in the initially excited rotational state ($v'=1$, $J'=\frac{3}{2}$) by tuning the uv laser to the $(R_{11}+Q_{21})(J'=\frac{3}{2})$ transition at $\lambda=223.847$ nm in the γ(1-1) band. Figure 2(c) shows the signal at this transition as the time delay between the ir and the uv lasers is changed. If the molecule-surface interaction time is short (compared with the microsecond time scale), the expected half-width should be less than 2 μs, similar to that in Fig. 2(b). There is, of course, a time delay due to the extra propagation distance. If we assume that there is no translational energy exchange and thus the beam velocity does not change after scattering, this delay time is about 50 μs, at the left arrow in Fig. 2(c). The other limit that one might assume is that the velocity of the molecule leaving the surface corresponds to the thermal energy characterized by the surface temperature, in which case one would also expect a broadening in time (right arrow). As one easily notices, neither of these peaks appeared. Since the population in the high-J'' states of $v''=0$ is known (see Fig. 1), one can compare the height of this line with those of nearby high-J'' lines ($\frac{63}{2}\leq J''\leq\frac{75}{2}$) of the $(R_{11}+Q_{21})$ branch in the γ(0-0) band to obtain an absolute calibration for

TABLE I. Scattering of vibrationally excited NO off LiF and CaF_2.

Surface	θ_i	E_n (cm^{-1})	θ_s	Beam excitation before surface	T_{surf}	Remaining in ($v'=1, J'=3/2$)	Transfer into ($v'=1, J'=11/2$)	Transfer into ($v''=0, J''=65/2$)
LiF	30°	1280	−10°	6×10^{-3}	300	$<2.3\times10^{-4}$	$<2.9\times10^{-4}$	···
					475	$<2.3\times10^{-4}$	···	$<1.4\times10^{-3}$
	30°	557	−10°	3.3×10^{-4}	300	$<2.9\times10^{-3}$	···	···
					520	$<6.3\times10^{-3}$	$<1.9\times10^{-3}$	···
CaF_2	15°	1600	+15°	8×10^{-4}	300	$<7\times10^{-3}$	···	···

the population in ($v'=1, J'=\frac{3}{2}$). If we assume the angular distribution for the vibrationally excited and the vibrationally unexcited (high-J'') molecules to be similar, the expected signal height would be about 4300 on the scale of Fig. 2(c), if no deactivation had occurred. The small, time-independent (in the microsecond scale) signal shown in Fig. 2(c) could be fully accounted for by the scattering of $v''=0$ molecules into this state. Thus, the incident, vibrationally excited molecules have been shown to be completely deexcited by the surface.

In search for a redistribution of the energy in the scattering of vibrationally excited molecules, we also performed similar time-delay measurements on other rotational lines of $v'=1$ and also on the $R_{21}(J''=\frac{65}{2})$ line of $v''=0$. This last state, having a similar internal energy ($E_{rot}=1817$ cm^{-1}) as the initially excited state ($E_{int}=1881$ cm^{-1}), is expected by the theoretical model[9] to be the dominant receiving state in the scattering process. We did not observe any measurable increase in population in either of these cases, nor in any other high-J'' lines of $v''=0$. The experimental results are summarized in Table I. Since we could not detect any ir-dependent signal, only a lower limit for the deactivation of ($v'=1, J'=\frac{3}{2}$) upon scattering with LiF and CaF_2 surfaces and upper limits for an energy transfer into ($v'=1, J'=\frac{11}{2}$) and ($v''=0, J''=\frac{65}{2}$) are given. These survival rates of vibrationally excited molecules are of similar magnitude as the survival rates reported recently for the scattering of metastable $He(2\,^1S)$ atoms off metal surfaces.[17]

We conclude that to a significant fraction (> 60%) the nonvibrating NO molecules undergo quasielastic scattering from the LiF surface. In contrast, vibrationally excited molecules get strongly deactivated. Under the assumption that no energy exchange with the surface takes place, about 10% of the molecules should undergo vibrational deactivation, according to the recent theoretical model calculation,[9] with the final state of the deactivated molecules being nearly exclusively that rotational state with the smallest energy gap with respect to the initially excited one.[9] Since in the scattering of $NO(v'=1, J'=\frac{3}{2}, \Omega'=\frac{1}{2})$ onto LiF and CaF_2 surfaces the vibrational energy did not show up as internal energy in the scattered molecules, the energy exchange with the surface is probably the dominant interaction process. However, the question of whether the energy is taken by the surface or transferred to the translation degree of freedom remains to be answered.

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Preliminary Determination of the Sun's Gravitational Quadrupole Moment from Rotational Splitting of Global Oscillations and its Relevance to Tests of General Relativity

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The sun's internal angular velocity is estimated from observations of rotational splitting of low-order, low-degree global oscillations detected as fluctuations in the limb-darkening function. The inferred rapid rotation implies a unitless grativational quadrupole moment, J_2, of $(5.5\pm1.3)\times10^{-6}$. When this result is combined with two published planetary radar results, values of 0.987 ± 0.006 and 0.991 ± 0.006 are obtained for $\frac{1}{3}(2+2\gamma-\beta)$, a quantity equal to 1 in the general theory of relativity.

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One test of theories of gravity concerns the precession of Mercury's orbit. After correction for Newtonian perturbations due to other planets, its predicted perihelion advance[1] (in arcseconds per century and ignoring preferred frame effects) is $42.95\lambda_p$, where

$$\lambda_p = \tfrac{1}{3}(2+2\gamma-\beta)+0.296J_2\times10^4. \qquad (1)$$

Planetary data determine λ_p, and β and γ are the Eddington-Robertson parameters in the parametrized post-Newtonian representation of the metric (see review by Will[1]) which are relevant at current accuracy levels. The quadrupole term in the gravitational potential is $-(GM/r)J_2(R/r)^2P_2$ for $r\geq R$, where G is the gravitational constant, P_2 the Legendre polynomial of order 2, and M and R the solar mass and radius.

The value of $\frac{1}{3}(2+2\gamma-\beta)$ varies from one relativity theory to another; in the general theory, for instance, it equals 1. This quantity's determination is central to planetary tests of general relativity. Equation (1) also makes clear that values for J_2 *and* λ_p are needed to determine $\frac{1}{3}(2+2\gamma-\beta)$. Anderson *et al.*[2] have found that J_2 and $\frac{1}{3}(2+2\gamma-\beta)$ cannot be separately determined, to a useful accuracy, from the available planetary data. To date, astrometric measurements of solar oblateness[3] have given the best inferred value of J_2.

Global solar oscillations offer a way to characterize the deep interior of the sun more directly. In particular, rotational splitting of otherwise degenerate nonaxisymmetrical modes provides averages of the interior solar angular velocity Ω. A sufficient variety of modes, each weighting Ω differently, can define the variation of Ω with position, allowing an improved estimate of the dynamical contribution to J_2. Bos and Hill[4] have resolved individual solar eigenstates in the period range 10 min to 2 h. We report here a preliminary value for J_2 based on these observations.

If one assumes slow rotation and $\Omega(r)\hat{k}$ as the rotational frequency, where $\hat{k}$ is the unit vector along the solar axis of rotation, the frequency of the (nlm) mode, given by Hansen, Cox, and Van Horn[5] is

$$\nu_{nlm}=\nu_{nl0}+\nu_{nlm}', \qquad (2)$$

with respect to an inertial frame of reference,