slope of the data in Fig. 3.

In conclusion, this Letter reports the first direct measurement of the distribution function of electrons accelerated solely due to resonant absorption. These electrons constitute a very low-density, high-energy component of the distribution function, which falls off exponentially at high energy. The decay constant K [$\Delta f \sim \exp(-W/K)$] increases linearly with the field strength to field width ratio of the localized resonant field. Calculations using a simple model of the field agree with these low-power experiments and suggest that the high-energy tail studied here is cut off at higher electron energies, falling off exponentially with the decay constant of the resonant electrons incident on the field. Higher-power experiments will resolve Δf at higher electron energies to test this prediction.

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Role of Rotational and Translational Local Modes in Vibrational Relaxation in Solids: A Study of NH and ND in Solid Ar

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A quantitative model for vibrational relaxation of impurity molecules in host crystals is presented, and applied to the vibrational relaxation of NH and ND in solid Ar. Realistic impurity-host interaction and impurity-cage geometry are employed. It is shown that impurity rotation is the dominant receiving mode in the relaxation, and only a small fraction of the energy released goes directly into phonon modes. The results explain the faster relaxation of NH compared with ND and the temperature independence of the measured decay rates.

The important recent progress in experimental studies of vibrational relaxation of impurity molecules in solids[1] led to observation of several interesting effects that could not be interpreted with existing theoretical models[2-5] in this field. Several difficulties arose: (1) It was found that deuterides generally relax more slowly than the corresponding hydrides [e.g., NH($A^3\Pi$, $v = 1$) and ND in Ar[6]; NH($\chi^3\Sigma^-$, $v = 1$) and ND in Ar[7]; CH_3F($v = 1$) and CD_3F in Kr[8]]. This result is in marked contrast with the theoretical prediction that the relaxation rate should decrease with an increase of the vibrational-energy gap.[2-5] (2) The experimental relaxation rates were found to be temperature independent or weakly T dependent. The theoretical models mentioned above involve multiphonon interactions, and as a consequence yield a strong temperature dependence. (3) The models referred to are semiquantitative and contain undetermined parameters. Attempts to calculate rates by substitution of realistic values for the parameters give rates that are too small by many orders of magnitude in most cases. The purpose of this Letter is to present a model that is free of the above-mentioned difficulties. Furthermore, we aim at providing a truly *quantitative* treatment of vibrational relaxation in solids, i.e., an approach that will calculate the relaxation rate from known and sufficiently accurate impurity-to-host atom interactions. The model that will be described is a major improvement over a previous recent treatment by Berkowitz and Gerber.[9] The limitation of the result of Ref. 9 is that it is based on an approximation that is not justified for most realistic systems. A key point of the present article is the application of the model to the calculation of vibrational relaxation of NH in solid Ar, the first quantitative treatment, so far as we are aware, of vibrational relaxation in solids.

Features of the model.—(i) As in Ref. 9, the three-dimensional (3D) geometry of the impurity cage is taken into account. For the system of NH (in the electronic ground state $X^3\Sigma^-$) in Ar, we assume that the impurity c.m. is located at a substitutional site in the fcc framework. Small static distortions of ~ 2% in the angles and distances of the nearest-neighbor atoms were introduced to represent the effect of the nonspherical impurity on the geometry around its site (the significance of this will be discussed later). Impurities in the electronic excited state may give rise to major distortions, the calculation of which is not feasible.

(ii) The potential causing vibrational relaxation will be taken as a sum of impurity–nearest-neighbor-atom interactions:

$$V=\sum_{i=1}^{p} V_i, \qquad (1)$$

where p is the number of nearest-neighbor atoms. Contributions of further atoms may have to be included in calculations of the lattice modes, but are too weak to influence relaxation directly. For V_i we assume the following form:

$$V_i=A_1\exp(-\alpha_1|\vec{r}_A-\vec{r}_i|)+A_2\exp(-\alpha_2|\vec{r}_B-\vec{r}_i|)+V_i^{\text{att}}, \qquad (2)$$

where the position vectors of the two impurity atoms are $\vec{r}_A$ and $\vec{r}_B$, and $\vec{r}_i$ is the position of the ith Ar neighbor. V_i^{att} is the long-range attractive part of the potential. A reliable NH-Ar potential is not available in the literature, but chemical similarity suggests that it should not differ much from the Ar-HCl potential (especially since the H-Ar component of the interaction affects the relaxation most). We fitted the form (2) to the Ar-HCl potential avialable from gas-phase data.[10] The assumption of the dumbbell form is essential, as it gives the high-order anisotropy components that play an important role in the relaxation (see below), and also the dependence of the potential on the vibrational coordinate of NH. The best fit to the potential of Ref. 10 was obtained with $A_1=213.3$ eV; $A_2=1852.05$ eV; $\alpha_1=2.82$ Å^{-1}; $\alpha_2=3.3$ Å^{-1} ($A\equiv$H atom; $B\equiv$N atom). Although $A_2>A_1$, the Ar-H interaction dominates in influencing the relaxation, since the heavier N atom is farther than the H from the nearest Ar neighbor. The direct contribution of the second and third terms in (2) to the relaxation will be neglected.

(iii) Local translational and resonance modes are calculated and included in the treatment as in Ref. 9. Local-mode contribution to the relaxation is expected to dominate over that of bulk modes[9] since the nearest-neighbor potential V varies most strongly with the local-mode coordinate. V of Eqs. (1) and (2) can be written in terms of creation and destruction operators pertaining to the various phonon modes[9]:

$$V\approx A_1\sum_{i=1}^{p}\exp(-\alpha_1|\vec{r}_{Ai}{}^0(\rho,\theta,\varphi)|)\times\exp\{-[D\sum_{\nu}C_\nu(b_\nu+b_\nu{}^\dagger)+C_L(b_L{}^\dagger+b_L)]\}, \qquad (3)$$

$\vec{r}_{Ai}{}^0$ is the distance vector from the H atom (A) to the ith Ar when the impurity c.m. and the lattice atoms are at equilibrium configuration; ρ is the internal vibrational coordinate of the impurity; θ and φ are the orientation angles of NH with respect to an arbitrary fixed axis; D is a quantity that can be computed from the dynamical matrix of the lattice[11]; the subscript L refers to the local mode, and ν refers to bulk modes. Also

$$C_\nu=\alpha_1(\hbar\omega_\nu/2N)^{1/2}, \quad C_L=\alpha_1(\hbar/\omega_L M)^{1/2}, \qquad (4)$$

with M the impurity mass and N the number of atoms. For NH in Ar we calculated a local mode of frequency $\omega_L=90$ cm^{-1}.

(iv) The rotational mode is included in the treatment. Rotational-mode participation as a receiving mode in vibrational relaxation was postulated by Brus and Bondybey[12] in order to interpret their experiments showing that hydrides relax faster than deuterides. Freed and Metiu[13] proposed a model in which vibrational energy is dissipated into a rotational mode, assumed to have a continuum of levels (without explicit phonon participation). In Ref. 9 and here we include the rotational mode *quantitatively*. Since NH in electronic ground state rotates freely,[7] we employed free-rotor states in our calculations. This is expected to be very accurate for high J levels. However, we tested the influence of using a librational wave function for $J=0$ (estimating a barrier height of $\sim 30\ \mathrm{cm}^{-1}$). The results were similar to those obtained with the $J=0$ free-rotor state.

Physical assumptions and approximations.—(a) We assume that the local mode is so narrow that its frequency is sharply defined (in some special cases this breaks down but can be augmented—see below).

(b) Since V of (3) depends much more strongly on the local translational mode than on the bulk phonons, we assume that the only multiphonon interactions that may contribute significantly are those involving the local mode. With regard to the bulk modes, only first-order contributions need to be considered. The energy difference $E_v+E_J-(E_{v'}+E_{J'})$ [(v,J) initial vibrational and rotational levels; (v',J') the final levels in a particular relaxation channel] is assumed to dissipate into $N_{JJ'}$ local phonons and the mismatch energy

$$\hbar\omega_v{}^* = E_v+E_J-(E_{v'}+E_{J'})-N_{JJ'}\hbar\omega_L \tag{5}$$

is emitted as a bulk phonon. For each pair (J,J'), $N_{JJ'}$ is rigorously defined.

With the above assumptions, one can evaluate the golden-rule expression for the following transition rate:

$$\Gamma_{i\to f}=\frac{2\pi}{\hbar}\underset{(i)}{\mathrm{Av}}\sum_f |V_{if}|^2\delta(E_i-E_f), \tag{6}$$

where $|i\rangle=|v,J,n_i,n_v\rangle$ and $|f\rangle=|v',J',n_f,n_v+1\rangle$; n_i and n_v refer to initial populations of the local and bulk modes; Av denotes the thermal averaging. Since the local mode has a high frequency, $n_i=0$, and $n_f=N_{JJ'}$. The derivation of a final working expression for $\Gamma_{i\to f}$ will be described in another publication[14]; here we only give the final result:

$$\Gamma_{v\to V'}=\underset{(JM)}{\mathrm{Av}}\sum_{J'M'}\Gamma_{vJM\to v'J'M'}, \tag{7a}$$

$$\Gamma_{vJM\to v'J'M'}=\pi\alpha_1{}^4A_1{}^2(D^2/\mu_I\omega_I)\Big[\sum_{i=1}^{p}F_{JM}{}^{J'M'}(i)\Big]^2\omega_v{}^*e^{C_L{}^2}(C_L{}^2)^{N_{JJ'}}/(N_{JJ'})!\,g(\omega_v{}^*)[\bar n(\omega_v{}^*)+1], \tag{7b}$$

where

$$F_{J'M'}{}^{JM}(i)=\int_0^{2\pi}\int_0^{\pi}P_{J'}(\theta)\exp[-iM'\varphi_e-\alpha|\vec{\mathrm{r}}_{Ai}{}^{0'}(\theta,\varphi)|]\,G_i(\theta,\varphi)P_J(\theta)e^{iM\varphi}\sin\theta\,d\theta\,d\varphi \tag{7c}$$

and G_i is a function that can be evaluated from the coordinates of the molecule and the equilibrium position of the ith atom. $\vec{\mathrm{r}}_{Ai}{}^{0'}$ is the distance of the A atom (H) to the ith Ar for $\rho=\rho_{\mathrm{eq}}$; μ_I and ω_I are the reduced mass and vibrational frequency of the impurity; $g(\omega_v{}^*)$ is the value of the phonon distribution function at the mismatch frequency, and $\bar n(\omega_v{}^*)$ is the population of that frequency.

The above result does not hold when $\omega_v{}^*=\omega_L$: Then, no bulk mode is involved and the final density of states comes from the *width* of the local mode. The result for such a situation, specialized to the case where only a single local phonon is emitted, is

$$\Gamma_{vJM\to v'J'M'}=\pi\,\frac{\alpha_1{}^2A_1{}^2}{\mu_I\omega_I}C_L{}^2\frac{g(\omega_L)}{\hbar}\Big|\sum_{i=1}^{p}F_{JM}{}^{J'M'}(i)\Big|^2. \tag{7d}$$

The results of the calculations on NH ($v=1$) and ND ($v=1$) are listed in Tables I and II. For gaining insight the values of the individual rotational components $\Gamma_{(v=1,J)\to(v=0,J')}$ (M' summed and M averaged) are given. The striking feature is that for both NH and ND the rotational mode is the overwhelmingly dominant receiving mode in the relaxation process. Vibrational relaxation is seen to populate very high J states ($J=13$ for NH). These populations then relax by coupling with phonons. The preferred final rotational state is the one nearest to compensating for the vibrational-energy gap, with only a small excess energy going into phonons. The dominant relaxation channel for NH involves one phonon only, and for ND three phonons. The contribution of high-order multiphonon process is totally negligible, and we believe that the conclusion as to the inefficiency of high-order multiphonon relaxation will be quite general for all impurities of large vibrational spacing, provided, at least, that

TABLE I. Relaxation of NH ($v=1$) in Ar at 15°K.

Transition	Rate ($\sec^{-1}$)	No. of local phonons	No. of bulk phonons
$(v=1, J=0) \rightarrow (v'=0, J'=13)$	2.4×10^{3}	1	0
$(v=1, J=1) \rightarrow (v'=0, J'=13)$	6.8×10^{4}	1	1
$(v=1, J=0) \rightarrow (v'=0, J=12)$	1.4×10^{-4}	5	1
$(v=1, J=1) \rightarrow (v'=0, J'=11)$	3.7×10^{-15}	10	1

there are no strong site distortions. The fact that relaxation of NH is faster than that of ND is due to the fact that the latter has less mass asymmetry giving rise to weaker rotational- (Coriolis-) coupling elements $F_{JM}^{J'M'}$. In addition, to achieve near resonance in ND, a higher final J' state is necessary than in NH, and this also implies weaker rotational-coupling elements $F_{JM}^{J'M'}$. The overall relaxation time calculated for NH is $\tau = 4.2 \times 10^{-4}$ sec. This is (given the complexity of the problem) in excellent agreement with Bondybey's experimental value $\tau = 1.9\times10^{-4}$ sec. Although in Table I we listed also transition rates with $J=1$ as the initial state, the contribution of the latter is negligible since the $J=1$ is not thermally populated at the temperature range of the experiment [(4–30)°K)]. For ND the decay time we compute $\tau = 0.49$ sec, which differs greatly from the experimental $\tau = 3.1\times10^{-2}$ sec, but Bondybey pointed out that the decay in ND is *radiative.* Hence experiment and theory are consistent in this case. The relaxation rate we calculated for NH is temperature independent since the dominant $(v=1, J=0) \rightarrow (v'=0, J'=13)$ transition involves only a *local* phonon, thermally unpopulated throughout experimental T range. Equations (7) will give some temperature dependence for systems that have a moderate mismatch frequency ($\hbar\omega_v{}^* \lesssim kT$). However, such a T dependence will be mild in comparison with that predicted by multiphonon models of vibrational relaxation. Finally, we draw attention to the importance of introducing small distortions ($\leq 2\%$ in the angles) in this case. In the absence of any distortion the symmetry of crystal-field potential (1) and (2) will result in a vanishing rate for even-odd transitions in J [such as $(v=1, J=0) \rightarrow (v=0, J=13)$]. The distortion can be crudely estimated from the Ar-NH and Ar-Ar interactions and the result is not too sensitive to it.[14]

It is our belief that these results prove the feasibility of quantitative calculations of vibrational relaxation in solids. Further examples will be treated in forthcoming publications.

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TABLE II. Relaxation of ND ($v=1$) in Ar at 15°K.

Transition	Rate ($\sec^{-1}$)	No. of local phonons	No. of bulk phonons
$(v=1, J=0) \rightarrow (v'=0, J'=15)$	2.10	2	1
$(v=1, J=0) \rightarrow (v'=0, J'=14)$	6.7×10^{-6}	5	1
$(v=1, J=1) \rightarrow (v'=0, J'=13)$	3.0×10^{-8}	7	1
$(v=1, J=0) \rightarrow (v'=0, J'=12)$	1.4×10^{-15}	10	1

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Electron-Phonon Contribution to the Phonon Linewidth in Nb: Theory and Experiment

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We present theoretical calculations and experimental measurements of the phonon linewidth for Nb. The calculations employ the rigid muffin-tin approximation and a realistic band structure. The measurements were done at low temperature to minimize the contributions to the linewidth from phonon-phonon interactions. The calculations predict and experiments confirm strong electron-phonon coupling for the longitudinal phonon modes in the [110] direction.

The phonon linewidth contains very detailed information concerning the electron-phonon interaction. Allen[1] has shown that the electron-phonon contribution to the linewidth of a phonon having mode index i and crystal momentum $\vec{q}$, $\gamma_i(\vec{q})$, measures directly the contribution to the total phonon-mediated electron-electron coupling arising from this particular phonon. Thus the electron-phonon coupling parameter λ which determines the electronic mass enhancement and superconducting transition temperature[2] is simply a weighted average of the phonon linewidth,

$$\lambda = \sum_{\vec{q},i} \gamma_i(\vec{q}) / \pi N(E_F)\omega_i^2(\vec{q}),$$

where $N(E_F)$ is the density of states of one spin at the Fermi energy.[3] The spectral function[4] $\alpha^2(\omega)F(\omega)$, obtainable from tunneling measurements, may also be written as an average over the linewidth as

$$\alpha^2(\omega)F(\omega) = \sum_{\vec{q},i} \gamma_i(\vec{q})\delta[\omega - \omega_i(\vec{q})]/2\pi N(E_F)\omega. \quad (1)$$

Linewidth measurements are very important for Nb because Nb has the highest transition temperature of any element and because the tunneling measurements on Nb remain quite controversial.[5,6] Axe and Shirane,[7] Shapiro, Shirane, and Axe,[8] and Bobrovskii *et al.*[9] have measured phonon linewidths in Nb_3Sn, Nb, and Pb, respectively. These Nb and Nb_3Sn measurements were, however, limited to transverse modes and to frequencies less than twice the superconducting energy gap.

The linewidth can be calculated as a double Fermi-surface integral

$$\gamma_i(\vec{q}) = (\pi\hbar/2M_a) \sum_{\vec{k},\vec{k}'} \delta(E_{\vec{k}} - E_F)\delta(E_{\vec{k}'} - E_F) \times \delta(\vec{k} - \vec{k}' - \vec{q}) |M_{\vec{k},\vec{k}'}{}^i|^2, \quad (2)$$

where M_a is the atomic mass. The matrix element $M_{\vec{k},\vec{k}'}{}^i$ is given by $M_{\vec{k},\vec{k}'}{}^i = \int d^3r\, \psi_{\vec{k}}{}^*(\vec{r}) \epsilon_{\vec{k},\vec{k}'}{}^i \times \nabla V \psi_{\vec{k}'}(\vec{r})$, where $\psi_{\vec{k}}$ is an electronic wave function, ϵ is a phonon polarization vector, and ∇V represents the change in crystal potential due to the displacement of a single atom. In our calculations we have employed the rigid muffin-tin approximation[10] which has been applied to a number of systems[11,12] and which seems to predict the correct magnitude and trends for the average electron-phonon coupling strength in the transition metals.[13]

We have calculated $\gamma_i(\vec{q})$ throughout the Brillouin zone by performing the integrations indicated in Eq. (2). Each Fermi-surface integration extended over a mesh of 53 424 first-principles points at the Fermi energy. Values of $\gamma_i(\vec{q})$ were stored in 5200 bins chosen to fill the irreducible wedge of the phonon Brillouin zone. The results of our calculations (described below) indicated considerable variation in $\gamma_i(\vec{q})$ as a function of