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*X*H defects in nonmetallic solids: General properties of Morse oscillators

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As part of a program to investigate light-atom vibrations associated with defects in nonmetallic solids, we have developed a general, dimensionless procedure to solve for the energy levels, wave functions, and transition-matrix elements for Morse oscillators. We can thus readily investigate transition-strength anomalies associated with electrical anharmonicities such as those recently observed in certain OH^- and OD^- systems in alkali halides. A center-of-mass correction in adapting the OH^- dipole moment function to OD^- is of central importance in interpreting isotope effects on fundamental and overtone transition strengths.

Introduction. The physics and chemistry literature is replete with accounts of the infrared properties of systems involving hydrogen attached to a heavier atom, commonly called *X*H systems.[1–15] Such systems may be diatomic or more complex molecules, hydrogen attached to a surface, or hydrogen-related defects in solids. This work has led to several general conclusions, among which are the following: first, hydrogen is sufficiently light that anharmonicity in the *X*H bond must be taken into account; second, a model of a free diatomic system is a fair first approximation for obtaining vibrational frequencies, but for some properties the environment plays an important role; third, electrical anharmonicity in the electric dipole moment is a crucial feature in determining the strengths of fundamental and overtone infrared bands.[15]

In 1991 Fowler, Capelletti, and Colombi[15] published a theoretical technique to deal with this problem, focusing particularly on OH^- and its isotopes in insulating solids. They introduced a reasonable, but *ad hoc*, treatment of such systems as single Morse oscillators[16] whose reduced mass depends on the coupling of the heavy atom to the environment. Within this effective Morse oscillator model, they investigated electrical anharmonicity effects in the framework of the Sage[17] form of the electric dipole moment function, and noted ranges of Sage's parameters which could yield unexpectedly strong overtones or weak fundamental IR absorptions. They applied this technique to OH^- and its isotopes in a variety of systems, including defect complexes[6] in alkali halides.

More recently Luty and co-workers[18] have greatly expanded the available data on such systems by investigating fundamental and overtone spectra of OH^- and OD^- in 15–20 alkali halide hosts. They have found both regularities and anomalies in their observed data, with particular anomalies occurring in connection with some of the IR absorption strengths.

In view of these results, and of the likelihood of a further explosion of data associated with the importance of hydrogen-related defects and the availability of high-resolution Fourier transform infrared spectrophotometers, we have been motivated to develop an analysis technique that would be both generic and easily applied. This paper discusses that technique and some applications.

Theory. Our goal is to develop a simple, accurate, general and easily applied technique to analyze IR spectra of *X*H systems. We will thus make some approximations which, although not necessary, are desirable in the interest of simplicity. For example, because the model of a free diatomic is rather accurate for determining energy levels,[15] we will use that approximation. We will also use a Morse potential to simulate the anharmonic *X*H bond. This is consistent with a wide array of literature; Morse potentials are used even for states of large quantum number, while our applications will all involve transitions from the $n=0$ state to $n=1$, 2, or 3.

Since we are using a Morse potential, we could in principle obtain analytical solutions for the Schrödinger equation as well as for the matrix elements necessary to analyze the transition probabilities. We have instead chosen to carry out these calculations numerically, solving the time-independent Schrödinger equation using a Runge-Kutta algorithm. There are several reasons for this, the main one being the ease with which dipole moment functions and anharmonic potentials of arbitrary form could be used as desired. The existence of analytical values for energies and moments has allowed us to check our results, and in general there is agreement in these quantities to within a few hundredths of a percent.

The computer code was written in Turbo Pascal. The code was designed with particular attention to versatility and reusability. To meet this specification, object-oriented code was used. The final version is menu-driven and is easily modified as desired.

The Morse potential is given by

$$V(R)=D_e\{\exp[-\beta(R-R_e)]-1\}^2 , \tag{1}$$

where R_e is the equilibrium separation and D_e and β are constants. The exact solution of the Schrödinger equation yields term values given by

$$G(n)=\omega_e[n+\tfrac{1}{2}][1-x_e(n+\tfrac{1}{2})] , \tag{2}$$

where

$$\omega_e=\beta(D_e/2\pi^2\mu c^2)^{1/2} , \tag{3}$$

$$\omega_e x_e=\hbar\beta^2/4\pi\mu c , \tag{4}$$

and μ is the reduced mass of the system. Note that in Eqs. (3) and (4) ω_e is expressed in wave numbers, while D_e is an energy. Thus, for example, if we choose as sample values $D_e=3$ eV, $\beta=2$ Å^{-1}, and $\mu c^2=9.3\times10^8$ eV, then $\omega_e=2556.7$ cm^{-1} and $x_e=0.0264$.

Reference 15 discusses various ways to combine these expressions with experimental data to determine the relevant parameters. Measurement of the fundamental and the first overtone for a given system leads to a determination of ω_e and x_e. Combining Eqs. (3) and (4) then yields an expression for D_e:

$$D_e=(\omega_e/x_e)(\pi\hbar c/2) \tag{5}$$

and for a combination of β and μ:

$$\beta^2/\mu c^2=4\pi\omega_e x_e/\hbar c\ . \tag{6}$$

Further information about the reduced mass can come from measurements on isotopes. For example, by comparing the wave number for the fundamental transition of an XH system to that of an XD system, one can determine the ratio of the reduced masses of these two systems. The ratio can be tested against various force-constant models for the defect. As noted above, in the present analysis we treat the system as a free diatomic, in which case the reduced masses are known.

In the present calculations we write a reduced and dimensionless form[19] of the Schrödinger equation as

$$\Psi''=\eta[v(x)-\varepsilon]\Psi\ , \tag{7}$$

where x is a dimensionless distance given by

$$x=\beta(R-R_e)\ , \tag{8}$$

ε is a dimensionless energy given by

$$\varepsilon=E/D_e\ , \tag{9}$$

$v(x)$ is a dimensionless Morse potential given by

$$v(x)=(e^{-x}-1)^2\ , \tag{10}$$

and η is a dimensionless parameter which by combining D_e, β, ω_e, and x_e we may write as

$$\eta=1/(4x_e^2)\ . \tag{11}$$

Finally, combining the above equations, we may write the dimensionless energy ε as

$$\varepsilon_n=4x_e[n+\tfrac{1}{2}][1-x_e(n+\tfrac{1}{2})]\ . \tag{12}$$

We thus have arrived at a very convenient working version of the Schrödinger equation for the Morse problem, with only one parameter. And this parameter, x_e, is one that in practice does not vary much for a given XH in different environments. Thus we expect that by choosing a single representative value of x_e for XH we may concentrate on this single generic version of the problem. The corresponding value of x_e for XD may be obtained by noting that x_e is proportional to $\mu^{-1/2}$, where the reduced mass μ is calculated for the pertinent diatomic system (e.g., OH$^-$ or OD$^-$).

There are two possible ways to treat the dipole moment function to be used in calculating transition probabilities: one, as a Taylor expansion in x, and two, as some analytical function such as that used by Sage.[17] The Sage function, written in terms of x, is

$$S(x)=k(x+\beta R_e)\exp(-x/\beta R^*)+C\ . \tag{13}$$

β and R_e are Morse potential parameters introduced in Eq. (1), while R^* is a new parameter which defines the detailed shape of the Sage function and C is an additive constant.

A final crucial point in utilizing the dipole moment function is to recognize that for a molecule that has a net charge the dipole moment must be expressed relative to the center of mass of the molecule.[1,20] This means that the dipole moment functions for, e.g., XD$^-$ and XH$^-$, will not be the same. Rather, there will be a difference which is linear in x. The Appendix shows that for a free diatomic molecule with net charge $-|e|$ the difference in dipole moments is given by

$$\Delta p\equiv p_{XD}-p_{XH}=|e|RM_X\left[\frac{M_D-M_H}{(M_H+M_X)(M_D+M_X)}\right]\ , \tag{14}$$

where p is the electric dipole moment and R is the hydrogen-X separation.

Applications to OH$^-$ and OD$^-$. Application of the results of the preceding section begins with an expression for p_{OH} as a function of x, and a corresponding expression for p_{OD} which differs from p_{OH} according to Eq. 14. Using values of oxygen, hydrogen, and deuterium masses for this case, we find

$$\Delta p=0.0523|e|R\ . \tag{15}$$

In terms of x this becomes

$$\Delta p=(0.0523|e|/\beta)(x+\beta R_e)\ . \tag{16}$$

To calibrate this correction in terms of our dimensionless units, we have approximately fitted the Werner, Rosmus, and Reinsch[20] center-of-mass dipole moment function for free OH$^-$ to a quadratic, obtaining

$$p_{OH}=0.383+0.3225R-0.1656R^2\ , \tag{17}$$

where R is in atomic units. Then the corresponding dipole moment function for OD$^-$ would be

$$p_{OD}=0.383+0.3748R-0.1656R^2\ . \tag{18}$$

To convert these to dimensionless units we use typical values of $R_e=1.82$ a.u. and $\beta=1.18$ a.u.$^{-1}$. Then

$$R=0.8475x+1.82 \tag{19}$$

and

$$p_{OH}=0.4214-0.2375x-0.1189x^2\ , \tag{20}$$

$$p_{OD}=0.5166-0.1932x-0.1189x^2\ . \tag{21}$$

We next expand the Sage function [Eq. (13)] to second order in x, with $\beta R_e=2.1476$ as above, and set R^*, k, and C to agree with Eq. (20). This yields $C=-0.8759$, $k=0.6041$, and $\beta R^*=1.5415$ to simulate free OH$^-$.

TABLE I. Transition matrix elements for OH^- and OD^-, computed from solutions of Eq. (7).

	OH^- matrix elements for $x_e = 0.021904$.			OD^- matrix elements for $x_e = 0.01595$.		
	$0\rightarrow1$	$0\rightarrow2$	$0\rightarrow3$	$0\rightarrow1$	$0\rightarrow2$	$0\rightarrow3$
x	−0.149 605	−0.015 998	0.002 825	−0.127 290	−0.011 549	−0.001 725
x^2	−0.016 844	0.029 444	−0.007 887	−0.010 356	0.021 772	0.004 916
x^3	−0.011 822	0.006 211	0.006 132	−0.006 975	0.003 280	−0.004 135
x^4	−0.002 770	0.005 343	0.001 839	−0.001 207	0.002 642	−0.000 867
x^5	−0.001 651	0.001 931	0.002 238	−0.000 668	0.000 708	−0.000 954
x^6	−0.000 579	0.001 269	0.001 121	−0.000 177	0.000 419	−0.000 352

Free OD^- is then simulated by the same expression with $(0.0952+0.0443x)$ added as the center-of-mass correction. We note that the constant term will not contribute to transition-matrix elements.

While applying these results to a variety of OH^- and OD^- systems, we realize that the coefficient of x in the additive term in Δp may depend on the environment and the bonding of OH^- or OD^- in a particular case. However, we have insufficient information to judge the amount of such a variation and so take the simplest route of assuming that the value appropriate to free OH^- is a reasonable one to use for other situations.

The expression for p_{OH} may be obtained in one of several ways: (1) One may use the Sage expression[17] in terms of x, and vary the parameter R^* to simulate different conditions. (2) One may express the dipole moment function as a power series[21] in x and vary the coefficients. (3) One may combine (1) and (2) by expanding the Sage function in a power series in x. In this case the coefficients will be related through the parameter R^*. In case (1) one would compute transition elements of the Sage operator between states of interest, while in cases (2) and (3) one would compute transition elements of powers of x.

For those wishing to utilize the results of this paper for cases of interest to themselves, methods (2) or (3) are probably the most readily applied. Hence we have computed, and present in Table I, transition-matrix elements of x, x^2, x^3, x^4, x^5, and x^6 for $0\rightarrow1$, $0\rightarrow2$, and $0\rightarrow3$ transitions of OH^- and OD^-, computed using the "typical" values $x_e = 0.021904$ for OH^- and 0.015950 for OD^-.

Since the transition probability from the ground state to higher states is proportional to the energy difference times the square of the dipole moment matrix element between these states, ratios of overtone-to-fundamental transition probabilities are readily computed using a given dipole moment function and the energy expression of Eq. (12). Figure 1 shows the result of such calculations. Shown are ratios of $0\rightarrow2/0\rightarrow1$ and $0\rightarrow3/0\rightarrow1$ transition probabilities for OH^- and for OD^-, as a function of the Sage parameter R^*. In this calculation the Sage function for OH^- was computed using $k = 0.6041$ and $\beta R_e = 2.1476$. The Sage function for OD^- has the same values of k and βR_e but also contains the additive term $0.0443x$. These values of the constants yield a good fit to the free-OH^- dipole moment function when $\beta R^* = 1.5415$, as discussed in the preceding section, and so effects of the environment are assumed to be accounted for by varying R^*.

These results are quite striking. As discussed in Ref. 15, the overtone-to-fundamental absorption-strength ratio is strongly dependent on R^*. Thus one might expect rather different results for OH^- and OD^- in different environments. For a given environment, however, one expects R^* to be fixed, and so Fig. 1 predicts particular sets of overtone and isotope data for given values of R^*, and may be very useful in analyzing experiments such as those discussed in Refs. 15 and 18.

For example, Luty and co-workers[18] found third and second harmonics of comparable strengths for OH^- in a number of alkali halides. We note that the corresponding curves in Fig. 1 cross for $R^* \approx 0.77$ Å, suggesting similar values of R^* for these cases. Luty and co-workers also found a very weak second harmonic for OH^- in LiF; this would suggest a smaller value of R^*, say of order 0.73 Å. They found the second-to-fundamental strength ratio to be consistently larger for OD^- than for OH^-: this is consistent with a large range of R^*, from 0.7 to 0.95 Å. And they found for OD^- in NaBr and KF that the second harmonic is from 3 to 7 times the strength of the fundamental. According to Fig. 1, this would be possible if R^* were around 0.88 or 0.93 Å.

These remarks do not mean that this approach, with the Sage dipole moment function, fits all the cases studied by Luty and co-workers. Indeed, detailed differences persist which may require a different dipole moment function or a different linear term in the center-of-mass iso-

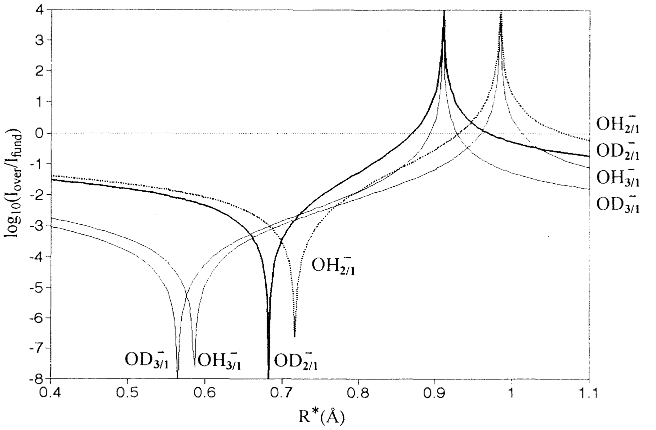

FIG. 1. Computed overtone-to-fundamental absorption intensity ratios versus R^*, on a $\log_{10}$ scale, using the Sage dipole moment function and solutions of the dimensionless Morse potential problem with anharmonicity parameter $x_e = 0.021904$ for OH^- and 0.015950 for OD^-. The Sage constants are $k = 0.6041$, $\beta R_e = 2.1476$. The Sage function for OD^- contains the additive term $0.0443x$, as discussed in the text.

tope shift. Furthermore, the physics of such large differences in dipole moment functions in different hosts is largely unexplored. It was noted by Wedding and Klein[1] that the shape of the dipole moment function of OH^- implies significant movement of electronic charge from oxygen to hydrogen as the O-H separation increases. It is likely that this type of effect will be sensitive to the environment of OH^-. Calculations by Hermansson[22] on OH^- in external electric fields show that vibrational frequencies and dipole moment derivatives, along with other properties, are strongly field dependent. Extensions of such calculations might provide the physical insight needed to understand the variety of results for OH^- in ionic hosts.

Summary. By computing the solutions of the Morse potential Schrödinger equation in dimensionless form, and corresponding transition-matrix elements for different powers of x, we have obtained results which may be applied to a variety of specific problems. Inclusion of the proper center-of-mass shift associated with H and D isotopes yields results which appear consistent with certain of the outstanding and unusual experimental features recently reported by Luty and co-workers for OH^- and OD^- in alkali halides.[18] In the process we have shown that electrical anharmonicity may explain in a natural way aspects of transition strengths which otherwise are quite inexplicable.

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APPENDIX

The dipole moment $\mathbf{p}$ for an array of charges q_i at positions $\mathbf{r}_i$ is given by

$$\mathbf{p}=\sum_i q_i \mathbf{r}_i \tag{A1}$$

with respect to the origin of coordinates. We may rewrite this in terms of center-of-mass and relative coordinates $\mathbf{R}_{\text{c.m.}}$ and $\mathbf{r}'_i$, where

$$\mathbf{r}_i=\mathbf{R}_{\text{c.m.}}+\mathbf{r}'_i \; ; \tag{A2}$$

$$\mathbf{p}=\mathbf{R}_{\text{c.m.}}\sum_i q_i+\sum_i q_i \mathbf{r}'_i \; . \tag{A3}$$

The second term in Eq. (A3) will lead to the dipole moment as a function of the nuclear separation for a diatomic system, measured with respect to the center of mass and computed quantum-mechanically as, e.g., by Werner, Rosmus, and Reinsch.[20] The first term is simply the position of the center of mass times the total charge of the system. For a fixed origin this term is a constant and so will not contribute to the infrared transition probability. However, for a nonfixed origin (such as one of the atoms) this term is not constant. For example, if the origin is on the X atom in XH^-, the center of mass is given by

$$\mathbf{R}_{\text{c.m.}}=[M_{\text{H}}/(M_{\text{H}}+M_X)]\mathbf{R} \; , \tag{A4}$$

where the relative coordinate $\mathbf{R}$ is given by

$$\mathbf{R}=\mathbf{r}'_{\text{H}}-\mathbf{r}'_X \; . \tag{A5}$$

This was noted by Werner, Rosmus, and Reinsch, who transformed their computed dipole moment centered on atom X (oxygen in their case) to the proper dipole moment centered at the center of mass by the equation

$$\mathbf{p}_{\text{c.m.}}=\mathbf{p}_X+|e|\mathbf{R}M_{\text{H}}/(M_{\text{H}}+M_X) \; , \tag{A6}$$

where the charge associated with the additive term is consistent with a net charge $-|e|$ of XH^-. (Thus for a neutral molecule this term would be zero and the location of the origin would not be important.) Equation (14) in the text results from the difference between the expression (A6) computed for XD^- and that computed for XH^-.

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