JOURNAL OF MOLECULAR SPECTROSCOPY **156**, 8–14 (1992)

Radial Functions of the Molecular Cation ArH$^+$ $X^1\Sigma^+$ from Vibration–Rotational Spectra

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The coefficients c_j, $0 \leqslant j \leqslant 9$, defining the potential energy $V(z)$ and six coefficients of four other radial functions related to adiabatic and nonadiabatic effects have been determined for the diatomic molecular cation ArH$^+$ in its electronic ground state $X\ ^1\Sigma^+$ by a direct fit to 331 experimental frequencies and wavenumbers of pure rotational and vibration–rotational transitions. Valid in the range of internuclear distance $1.0 < R/10^{-10}$ m < 2.0, these functions serve to reproduce the reported wavenumbers of the transitions within 1.2 times the uncertainties of the measurements. Comparisons are made with previous analyses of these spectral data.

INTRODUCTION

To measure directly the frequencies and wavenumbers of pure rotational and vibration–rotational transitions of diatomic molecular ions is becoming increasingly practicable. Despite their relatively small concentrations in the steady state within the reaction vessel in which their spectra are measured and their transitory existence unless an electric discharge is maintained, in particular the cations formed from a noble gas atom and either a proton or deuteron (or equivalent reactants) have been extensively investigated in both emission and absorption. Data are thus available for the chemical family HeH$^+$ to XeH$^+$, but the compound for which spectral data are most abundant is ArH$^+$. In this case 12 pure rotational (*1–5*) and 319 vibration–rotational transitions (*6–8*) have been measured. Most spectral lines belonged to the abundant isotopic variant ^{40}Ar^{1}H$^+$, but some lines of ^{40}Ar^{2}H$^+$, ^{36}Ar^{2}H$^+$, ^{38}Ar^{2}H$^+$, ^{36}Ar^{1}H$^+$, and ^{38}Ar^{1}H$^+$ were also measured either as a result of deliberate introduction of deuterium into the system of production or as fortuitous observations of lines of the two rare isotopes of Ar in natural abundance. These data enable the determination of the radial functions that constitute not only the most physically meaningful representation of the data but also the most compact (*9*).

Our determination proceeds directly from the measured wavenumbers of the pure rotational and vibration–rotational transitions to the functions of the internuclear distance for not only the potential energy but also the adiabatic and nonadiabatic effects of diatomic molecules; our procedure is based on analytic relationships between the parameters of these functions and the energies of the vibration–rotational states within a particular electronic state. Expressed in the convenient form of truncated polynomials, these functions are useful to predict unmeasured transitions within, and even somewhat beyond, the range of energy of the measured transitions, but particularly for isotopic variants for which experimental data are lacking. Because data exist for transitions of isotopic variants of both the Ar and H atomic species, the available data of ArH$^+$ offer an attractive application of our procedure. We have previously applied this method to the vibration–rotational spectra of several neutral diatomic molecules,

0022-2852/92 $5.00

including a hydride species LiH (*10*) and a nonhydride SiS (*11*); in these cases the data of isotopic variants enabled the determination of several parameters related to the adiabatic and nonadiabatic effects in addition to the potential-energy function.

METHOD OF ANALYSIS

We recall here the salient features of the procedure as the basis of understanding its application to ArH^+. The effective potential energy governing the internuclear vibration and rotation (about the center of molecular mass) of a diatomic molecule within a particular electronic state of type ${}^1\Sigma$ that contains five radial functions is expressed (*10, 12*) as

$$V_{\mathrm{eff}} = c_0 z^2\Big(1 + \sum_{j=1} c_j z^j\Big) + \sum_{j=1} m_e h_j^{\mathrm{Ar}} z^j / M_{\mathrm{Ar}} + \sum_{j=1} m_e h_j^{\mathrm{H}} z^j / M_{\mathrm{H}} + B_e J(J+1)\Big[1 + \sum_{j=0} m_e g_j^{\mathrm{Ar}} z^j / M_{\mathrm{Ar}} + \sum_{j=0} m_e g_j^{\mathrm{H}} z^j / M_{\mathrm{H}}\Big] R_e^2/R^2, \qquad (1)$$

in which m_e is the electronic rest mass, M_{Ar} and M_{H} are the masses of the separate atoms of types Ar and H, and the reduced variable z for displacement of internuclear separation R from the equilibrium distance R_e is defined (*13, 14*) as

$$z \equiv 2(R - R_e)/(R + R_e). \qquad (2)$$

For the molecular cation ArH^+ the reduced mass is represented by the product of the atomic masses M_{Ar} and M_{H} divided by the total mass of the molecular ion,

$$\mu = M_{\mathrm{Ar}} M_{\mathrm{H}} / (M_{\mathrm{Ar}} + M_{\mathrm{H}} - m_e). \qquad (3)$$

The functions involving the coefficients $h_j^{\mathrm{Ar,H}}$ take empirically into account collectively mostly the adiabatic effects, that the potential energy depends on not only the relative separation of the nuclei but also their momenta, and the nonadiabatic effects related to the vibrational inertia of the electrons, because other effects have different dependences on atomic mass which makes them currently negligible with respect to the experimental error of frequency measurements (*12*). The functions involving the coefficients $g_j^{\mathrm{Ar,H}}$ take empirically into account predominantly the nonadiabatic effects of the rotational inertia of the electrons (*12*). The two nonadiabatic effects may be considered to arise from interactions between electronic states induced by the vibrational and rotational motions of the nuclei respectively. Defined according to Eq. (1), all coefficients c_j, $g_j^{\mathrm{Ar,H}}$, and $h_j^{\mathrm{Ar,H}}$ are formally independent of mass; only the coefficients c_0 and $h_j^{\mathrm{Ar,H}}$ are not dimensionless. Because the center of mass of the molecule varies with isotopic substitution (i.e., replacing ^{40}Ar by ^{36}Ar, for instance), there are only indirect correspondences between the individual empirical functions containing the coefficients $g_j^{\mathrm{Ar,H}}$ and $h_j^{\mathrm{Ar,H}}$ and the theoretical functions according to which one represents the specific adiabatic and nonadiabatic effects (*12*). Only according to the formal independence of mass of these coefficients can one determine empirically their values, but the result of that independence of mass is that the empirical functions consist of the theoretical effects, the vibrational nonadiabatic and adiabatic effects, or the vibrational and rotational nonadiabatic effects, combined in inseparable proportions. As a consequence of the various contributions to the effective potential energy, the vibration–rotational terms consist also of several contributions; the expression for these terms is an extension of Dunham's form (*15*)

$$E_{vJ} = \sum_{k=0} \sum_{l=0} \left(Y_{kl} + Z_{kl}^{h,\mathrm{Ar}} + Z_{kl}^{h,\mathrm{H}} + Z_{kl}^{g,\mathrm{Ar}} + Z_{kl}^{g,\mathrm{H}}\right)\left(v + \tfrac{1}{2}\right)^k (J^2 + J)^l, \qquad (4)$$

in which to simplify the notation we suppressed the explicit isotopic dependence of the vibration–rotational terms E_{vJ}, the coefficients Y_{kl}, and the various coefficients Z_{kl}. We suppose the coefficients Y_{kl} to result from purely the internuclear potential energy $V(z)$ and the centrifugal motion of the nuclei and associated electrons; the remaining coefficients, the four components of Z_{kl}, reflect respectively the obviously corresponding terms considered as perturbations separately additive in the effective potential energy according to Eq. (1).

Analytic expressions of the coefficients Y_{kl} as functions of the harmonic vibrational coefficient k_e (implicitly contained within $U_{1,0}$ or ω_e), the equilibrium separation R_e (implicitly contained within $U_{0,1}$ or B_e), the reduced mass μ, and the potential-energy coefficients c_j with $j \leqslant 10$ have been published in machine-readable form (*16*); further expressions containing coefficients with $j \leqslant 22$ have been generated according to hypervirial perturbation theory (*17*). The coefficient c_0 in Eq. (1) is defined in terms either of $U_{1,0}$ and $U_{0,1}$, such that $c_0 = U_{1,0}^2/(4U_{0,1})$, or equivalently of k_e and R_e, such that $c_0 = k_eR_e^2/(2ch)$; the fundamental physical constants c and h enter this relationship because E_{vJ}, Y_{kl}, and Z_{kl} are all expressed in units of wavenumber for spectral applications. Of the five parameters $U_{1,0}$, $U_{0,1}$, c_0, k_e, and R_e, all formally independent of mass, only two are independent; in our analysis $U_{1,0}$ and $U_{0,1}$ were determined directly and the others were derived subsequently therefrom. Each term coefficient Y_{kl} or Z_{kl} consists of contributions in series,

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \cdots\cdot , \tag{5}$$

$$Z_{kl} = Z_{kl}^{(0)} + Z_{kl}^{(2)} + \cdots , \tag{6}$$

independently of the method of generation of the actual expressions of the coefficients (or of the notation used to distinguish the contributions). If the leading contributions $Y_{kl}^{(0)}$ are expressed as a product with the reduced (atomic) mass μ,

$$Y_{kl}^{(0)} = U_{kl}\mu^{(1/2k+l)}, \tag{7}$$

the coefficients U_{kl} become formally independent of mass. Although we have derived some expressions of the contributions $Y_{kl}^{(6)}$, $Y_{kl}^{(8)}$, and $Y_{kl}^{(10)}$ containing coefficients c_j with $j \leqslant 22$, only the leading term $Y_{kl}^{(0)}$ and the first two corrections $Y_{kl}^{(2)}$ and $Y_{kl}^{(4)}$ are required because the effects of experimental error of measurements of frequencies and wavenumbers greatly exceed the magnitudes of further corrections. Analogously, for each component of Z_{kl} even the first correction $Z_{kl}^{(2)}$ is negligible for the present data; furthermore, we cannot include consistently additional terms without taking into account the interaction of the various effects. The auxiliary coefficients Z_{kl} in each set are functions of both the potential-energy coefficients c_j and the respective coefficients either g_j or h_j for nuclei of type Ar or H. The coefficients Y_{kl} depend on the parameters c_j in a strongly nonlinear manner, whereas the coefficients Z_{kl} depend on the parameters g_j or h_j linearly but c_j nonlinearly. A few expressions of Z_{kl}^h in terms of c_j and h_j have been already published in a different but equivalent form (*18*), which one can readily convert to be consistent with the present definition according to Eq. (1); a larger collection of expressions containing the coefficients h_j with $j \leqslant 10$ will be published in machine-readable form with the extended set of expressions of Y_{kl}. Likewise a few expressions equivalent to Z_{kl}^g have been reported (*12*); a larger collection containing g_j with $j \leqslant 10$ will analogously be published with Z_{kl}^h.

We apply the method of estimation of nonlinear parameters to determine the applicable coefficients c_j, $g_j^{\mathrm{Ar,H}}$, and $h_j^{\mathrm{Ar,H}}$ directly from the frequencies ν (converted to wavenumber units in m^{-1}) and wavenumbers $\tilde{\nu}$ of all available pure rotational and vibration–rotational transitions. The wavenumbers $\tilde{\nu}$ of the transitions are the difference of the two terms E_{vJ} of the combining states; the criterion of convergence of a fit to a particular model is that the sum of the squares of the residuals between the measured and calculated values, $\tilde{\nu}_{\mathrm{obs}} - \tilde{\nu}_{\mathrm{calc}}$, is a minimum, hopefully the global minimum (apart from possibly the united atom (*19*)). The algorithm of the fitting process employs the analytic expressions of not only the term coefficients Y_{kl} and the various components of Z_{kl} but also the first (partial) derivatives of Y_{kl} and Z_{kl} with respect to the parameters, for instance $\partial Y_{kl}/\partial c_j$, $\partial Y_{kl}/\partial U_{1,0}$ and $\partial Z_{kl}/\partial g_j$. The analytic expressions of the former derivatives with $j \leqslant 10$ have been already published in machine-readable form (*16*); expressions of further derivatives of Y_{kl} and of the derivatives $\partial Z_{kl}^{g}/\partial g_j$ and $\partial Z_{kl}^{h}/\partial h_j$ will form part of the large collection to be published subsequently in machine-readable form. The various dependences of the residuals on the masses M_{Ar}, M_{H}, and J make possible in principle the determination of the coefficients g_j^{Ar}, g_j^{H}, h_j^{Ar}, and h_j^{H}, although in practice the quality and quantity of available data may preclude the significant determination of coefficients of some types. To select among various models tested during the fitting procedure, involving varied numbers of coefficients in the prospective five functions, we employ the F-value as the criterion; this statistic takes into account both the number of degrees of freedom (number of data minus the number of fitting parameters) and the standard deviation of the fit. Each uncertainty in the table represents one estimated standard error, and the uncertainties in k_e and R_e take into account also the error in the pertinent fundamental constants (*20*). The atomic masses are drawn from the latest consistent set (*21*).

RESULTS

The 331 unduplicated spectral lines consisted of pure rotational transitions numbering eight for ^{40}Ar^{1}H$^+$ (*1, 3–5*), two for ^{40}Ar^{2}H (*2–5*), and one each for ^{36}Ar^{2}H$^+$ and ^{38}Ar^{2}H$^+$ (*2*), and vibration–rotational transitions numbering 275 for ^{40}Ar^{1}H$^+$ (*5–7*), seven for ^{36}Ar^{1}H$^+$ (*7*), two for ^{38}Ar^{1}H$^+$ (*7*), and 35 for ^{40}Ar^{2}H$^+$ (*6*) from the indicated sources. In the few cases in which duplicate measurements of particular lines were reported, the agreement was consistent with the nominal uncertainties of the measurements. The wavenumber of each transition was assigned a weight, equal to the reciprocal of the squared standard deviation or squared estimated uncertainty of the measurement. Table I displays the results of the fit of these data according to which seventeen independent parameters were determined significantly. As the data include transitions involving up to $v = 7$ (of only ^{40}Ar^{1}H$^+$), we were able to determine potential-energy coefficients c_j with $j \leqslant 9$. As the data include pure rotational and vibration–rotational transitions of both ^{40}Ar^{1}H$^+$ and ^{40}Ar^{2}H$^+$, we determined four parameters h_1^{H}, h_2^{H}, g_2^{H}, and g_3^{H}; in contrast, because data involving nuclides of Ar other than ^{40}Ar are relatively scarce, it proved practicable to determine only two coefficients h_1^{Ar} and g_1^{Ar}. Fits in which g_1^{H} was varied produced values near zero having a comparably small estimated standard error; for this reason the value of g_1^{H} was constrained to zero in succeeding fits. By means of this set of parameters, we reproduced the input frequencies and wavenumbers within 1.2 times (on average) the uncertainties of the experimental measurements specified by the particular authors; the deviations of only 10 data exceeded three specified uncertainties, none greater than 4.2 uncertainties, and more than half the lines (172/331) were reproduced within 0.6 stated

TABLE I

Coefficients of the Radial Functions and Other Molecular Properties of ArH$^+$ $X\,^1\Sigma^+$, All Independent of Mass

j	c_j	g_j^{Ar}	g_j^H	$h_j^{Ar}/10^6 m^{-1}$	$h_j^H/10^6 m^{-1}$
0	(17570562.8 ±18.8) m^{-1}				
1	-1.563863 ±0.000051	6.59 ±1.13	0.0	15.9 ±3.1	2.603 ± 0.032
2	1.19439 ±0.00025		-3.05 ±0.27		-19.909 ± 0.102
3	-0.59078 ±0.00122		2.87 ±0.62		
4	0.2045 ±0.0069				
5	0.1258 ±0.0150				
6	-0.712 ±0.094				
7	-0.433 ±0.40				
8	6.448 ±0.96				
9	-17.9 ±2.6				

$U_{1,0}$ = (268834.543±0.189) m^{-1} u$^{1/2}$

$U_{0,1}$ = (1028.31100±0.0025) m^{-1} u

k_e = (425.81472±0.00065) N m^{-1}

R_e = (1.2803716±0.0000019)x10^{-10} m

Range: $1.0 < R/10^{-10}$ m < 2.0

uncertainties of measurement. Because the distribution is approximately *normal*, we consider the fit to be statistically significant. Although there was evidence of slight systematic deviations of transitions of Ar^{2}H$^+$, no further coefficients g_j^H or h_j^H could be determined significantly.

DISCUSSION

For comparison with our fit of 331 transitions with 17 independent parameters, the first fit (*6*) of 240 vibration–rotational transitions of only ^{40}Ar^{1}H$^+$ with $v \leqslant 5$ required 19 parameters of the type Y_{kl}. A later fit (*7*) including with the former 240 lines 66 further vibration–rotational transitions and some rotational transitions (*1*, *2*) required either 22 parameters of the type Y_{kl} for the transitions of only ^{40}ArH$^+$ with $v \leqslant 7$ or 28 parameters of the types U_{kl} and $\Delta_{kl}^{Ar,H}$ for all the isotopic variants; the latter parameters are equivalent to the parameters $Z_{kl}^{h,Ar}$ or $Z_{kl}^{h,H}$ in Eq. (4) (*18*). Johns remarked (*7*) that the estimates of the error of his six parameters $\Delta_{kl}^{Ar,H}$ must be regarded as optimistic because they depended on few observations; the fact that only three parameters $h_j^{Ar,H}$, derived from Z_{kl}^h or Δ_{kl}, were determined in our work is consistent with those reservations. The determination by Johns of $Y_{5,1}$ and $Y_{6,0}$ or $U_{5,1}$ and $U_{6,0}$ would be equivalent to the determination of the potential-energy coefficients c_9 and c_{10}; in our work c_9 was significantly determined but attempts to determine c_{10} yielded of c_{10} large values, ~70, with not only a relatively large standard error, >30, but also much enhanced standard errors of other parameters c_j, $3 \leq j \leq 9$, compared with fits lacking c_{10}.

In their attempt to determine not only the potential-energy function but also functions for the adiabatic and nonadiabatic effects from 312 transitions of five isotopic variants, Gruebele *et al.* (*5*) claimed to determine 17 coefficients a_j, $0 \leq j \leq 16$, of Dunham's function (*15*), but only seven coefficients b_j, $0 \leq j \leq 6$, of the function proposed by Simons *et al.* (*22*). Because all these coefficients a_j, b_j, and c_j are readily interconvertible (*13*), clearly about 10 or 11 coefficients are required, not less than 10 nor more than 11 according to both our results and those of Johns (*7*), to reproduce almost all 331 spectral lines of six isotopic variants essentially within the precision of their measurement. For the potential energy expressed as a series of exponential terms (*5*), the so-called perturbed Morse oscillator, Gruebele *et al.* required 10 coefficients, consistent with the above number 10 for $V(z)$. These workers remarked that the parameters a_j, $0 \leq j \leq 8$, of Dunham's function $V(x)$ for potential energy failed to reproduce satisfactorily the observed wavenumbers of the spectral transitions; however, coefficients a_j with $j = 9$ or 10 are required according to the above analysis. If lines due to isotopic variants are included in the data set then further parameters, preferably equivalent to g_j and h_j of the separate atomic types Ar and H, are also required, as our results demonstrate unequivocally; the relatively poor definition of some such coefficients, like the deviations of the Ar^2H^+ transitions, reflects the dominance of lines of $^{40}Ar^1H^+$ in the data set.

In the attempt by Gruebele *et al.* (*5*) to generate some radial functions for the adiabatic and nonadiabatic effects, 10 further parameters were claimed to be determined. One such parameter "$g_v^e(R_e)$" is related to the vibrational nonadiabatic effect; the theoretical discussions by Herman and Asgharian (*23*) and Watson (*24*) and our investigation (*12*) made clear that no such separation of the vibrational nonadiabatic and adiabatic effects is practicable, because effects of both types have exactly the same dependence on vibrational v and rotational J quantum numbers and on mass. Herman and Asgharian (*23*) stated that there exists *no* magnetic effect of low order by means of which even this single parameter to represent the vibrational nonadiabatic effects can be determined. Moreover the results of Gruebele *et al.* (*5*) demonstrate that, even for the value -0.000343 ± 0.000027 claimed to be determined for $g_v^e(R_e)$, the correlation coefficient between that and an important potential-energy parameter is -0.995; hence these two parameters are almost totally correlated and the purported value of $g_v^e(R_e)$ thus essentially entirely lacks significance, even if the adiabatic and vibrational nonadiabatic effects were separable (*23*, *24*). Their parameters $d_r^{H,Ar}$, $d_H^{(2)}$, and $d_H^{(4)}$ appear to correspond roughly to our parameters h_j^H. Gruebele *et al.* (*5*) claimed to determine two parameters G_1 and G_2 that appear to correspond to ours of type g_j^H or g_j^{Ar}; this number is less than that of our parameters g_1^H, g_2^H, and g_1^{Ar}. As their calculations (*5*) required four hours to execute on a supercomputer that carried only 12 decimal digits, the inadequate precision and the numerical nature of the algorithm perhaps misled these authors; if some rotational frequencies contain nine significant digits (*2*), clearly digits numbering more than twelve must be carried through computations involving those quantities. For comparison, computation of each model including our particular sets of parameters required about 20 min on a machine having a processing rate equivalent to that of a superior personal microcomputer but our calculations (mostly substitution of the analytic expressions and their derivatives) were executed carrying 32 decimal digits throughout. The values of both R_e and a_1 calculated by Gruebele *et al.* agree with those of R_e and $c_1 - 1$ respectively in the table, but for R_e their standard error is much larger than ours.

CONCLUSIONS

According to our analytic theory and with ample statistical indicators in the calculations, we have determined the parameters of five radial functions of ArH^+ that reproduce satisfactorily the 331 pure rotational and vibration-rotational transitions in our data set. The values of both the generated parameters and their estimated standard errors are presented in the table with the corresponding range of validity of the functions.

ACKNOWLEDGMENTS

I thank Dr. J. W. C. Johns of the National Research Council of Canada for kindly providing data, and the National Science Council of the Republic of China for financial support.

RECEIVED: February 7, 1992

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