

## On the dissociation energy and interaction potential of ground-state $\text{Ne}_2$

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(Received 7 February 1974 ; revised 10 April 1974)

### 1. INTRODUCTION

In recent studies of the  $\text{Ne}_2$  interaction potential [1-4], the beautiful spectroscopic measurements of Tanaka and Yoshino [5] were not fully exploited for testing the accuracy of the different functions proposed. Of these studies, Maitland's [3] was the only one to attack the rather difficult problem of combining the spectroscopic results with other types of experimental data (viscosities and second virial coefficients) in order to determine an optimum potential energy function. Unfortunately, he appears to have been unsuccessful, since the resulting function is not in good agreement with the observed vibrational level spacing. Indeed, it yields a worse estimate of this quantity than do the potentials derived from solid state properties by Goldman and Klein [1].

In other work, Tanaka, Yoshino, and Freeman [4] compared the spectroscopic properties of divers previously reported  $\text{Ne}_2$  potentials with the experimental observations [5]. However, we believe that their discussion was somewhat distorted by an erroneous 'experimental' estimate of the binding energy of level  $v = 1$ , which in turn led to an estimate of the ground-state dissociation energy  $D_0$  which is some 7 per cent too large. The present analysis of this question further supports the conclusion that the solid state potentials of Goldman and Klein [1] are the most reliable potential curves currently known for this species†.

### 2. SPECTROSCOPIC TEST OF $\text{Ne}_2$ POTENTIAL FUNCTIONS

Recent molecular beam scattering experiments [2] and the analysis of solid state properties [1] have greatly improved our knowledge of the  $\text{Ne}_2$  interaction. In particular, the ESMSV-type scattering potential obtained by Farrar and Lee, and the two solid-state MSV-type potentials of Goldman and Klein all predict differential scattering cross-sections, second virial coefficients, and solid state

† Goldman and Klein [1] derived two different MSV-type interaction potentials, their MSV-I being obtained from an analysis which considered only pairwise additive forces, while their MSV-II corresponds to the inclusion of Axilrod-Teller-Muto three-body forces in these calculations ; both are considered here.

properties (lattice spacing, sublimation energy and compressibility) in good agreement with experiment [2]. To be precise, we should note that the MSV curves are consistent with high temperature bulk properties only if the repulsive wall is modified at short range. In ref. [2] this was done by joining the curves with a spline function for the region  $R/R_m = 0.50-0.83$ , to the exponential:  $1.553D_e \exp[-12.44(R/R_m - 1)]$ . However, this modification does not change the potential well, and hence has no effect on its spectroscopic properties. Table 1 compares the spectroscopic properties of the above potentials with those of Maitland's MMV curve [3], and with experiment [5].

	Expt. [5]	MMV[3]	MSV-I[1]	MSV-II[1]	ESMSV[2]	Recommended
$G(0)$	—	11.18	12.19	12.45	12.56	12.3 ( $\pm 0.2$ )
$\Delta G_{1/2}$	13.7 ( $\pm 0.5$ †)	12.97	13.61	14.07	14.32	13.7 ( $\pm 0.5$ )
$D-G(1)$	(3.7 ?)	3.37	2.49	2.68	2.82	2.6 ( $\pm 0.2$ )
$D-G(2)$	—	0.022	0.004	0.008	0.011	$\lesssim 0.01$
$D_0$	17.4( ?)	16.34	16.10	16.75	17.14	16.3 ( $\pm 0.7$ )
$D_e$	—	27.52	28.29	29.20	29.70	28.6 ( $\pm 1.0$ )
$B_0$	0.16–0.18	0.153	0.155	0.156	0.155	—
$B_1$	—	0.104	0.098	0.099	0.101	—
$h_6$ ‡	—	1.25	1.25	1.25	1.25	—

† Since no uncertainty was reported, this value is estimated.

‡ Height of the centrifugal barrier for  $J=6$ .

Table 1. Spectroscopic properties of ground-state  $\text{Ne}_2$  (all quantities in  $\text{cm}^{-1}$ ).

### 2.1. Spectroscopic observables

Of the three observables, the rotational constant  $B_0$  is clearly the least selective, since the calculated values for all four potentials are in equivalent agreement with experiment. However, consideration of the vibrational spacing  $\Delta G_{1/2}$  clearly shows that the two MSV potentials are much more satisfactory than the MMV or ESMSV curves. Furthermore, all of the other functions considered in [4] have  $\Delta G_{1/2}$  values which are significantly larger than any of those in table 1, and hence in significantly worse agreement with experiment.

In contrast to the  $\Delta G_{1/2}$ , the experimental value of the  $v=1$  binding energy  $D-G(1)$  appears to discriminate against the MSV potential. However, we believe that this is due to error in the 'experimental' estimate of the  $v=1$  binding energy.

The  $3.7 \text{ cm}^{-1}$  binding energy given in [4] was based on three assumptions: (i) that the highest bound or quasibound level associated with  $v=1$  is  $J=6$ , (ii) that the centrifugal potential barrier for  $J=6$  is  $1.25 \text{ cm}^{-1}$  high, and (iii) that the  $v=1$  rotational constant is  $B_1=0.10 \text{ cm}^{-1}$ . However the results in tables 1 and 2 show that *all three of these assumptions are in fact satisfied by the two MSV potentials* whose  $v=1$  levels are bound by only  $2.49$  and  $2.68 \text{ cm}^{-1}$  respectively. The anomalous size of the previous estimate is seen as having two sources. On the one hand, it was apparently assumed that all of the rotational energy was accounted for by the single rotational constant  $B_1$ : the results in table 2 show that this is not true. In addition, it appears that a fairly cautious assumption

$v$	$J$	MSV-I	MSV-II
1	0	-2.49	-2.68
1	1	-2.30	-2.48
1	2	-1.19	-2.08
1	3	-1.35	-1.51
1	4	-0.62	-0.76
1	5	0.22 (<0.01)	0.12 (<0.01)
1	6	1.14 (0.22)	1.06 (0.16)

Table 2. Level energies (in  $\text{cm}^{-1}$ ) of the Goldman-Klein MSV potentials; the zero of energy is the dissociation limit†.

† The quasibound levels were located using the Airy function boundary condition of ref. [6] while, their widths (given in parentheses) were calculated semiclassically.

was made about the proximity to the barrier maximum of the last quasibound level. The fact that this last level is measurably broadened for the two MSV potentials does not rule against their being observed, since an experimental resolution of around  $0.0005 \text{ \AA}$  would have been required to resolve this broadening. In conclusion, the fact that the MSV functions accurately reproduce a wide range of other experimental data, in addition to having the best  $\Delta G_{1/2}$  values of any potentials considered to date†, implies that their  $v=1$  binding energies should provide reasonably reliable estimates of this quantity. This is the source of the 'recommended' value  $2.6 (\pm 0.2) \text{ cm}^{-1}$  given in table 1.

An independent estimate of the  $v=1$  binding energy was obtained by Maitland [3] using the 'near-dissociation' method of analysing vibrational spacings, which had previously been applied to  $\text{Ar}_2$  [9] and  $\text{Kr}_2$  [10]. According to this approach, the experimental  $\Delta G_{1/2} = 13.7 (\pm 0.5) \text{ cm}^{-1}$  implies that  $[D - G(1)] = 2.9 (\pm 0.4) \text{ cm}^{-1}$ ‡. The earlier [9, 10] results for  $\text{Ar}_2$  and  $\text{Kr}_2$  suggest that such an estimate will be a lower bound to the true value of this binding energy. However, application of this technique to the exact calculated  $\Delta G_{1/2}$  values for all but one of the nine potential curves considered here and in ref. [4] (the exception being Maitland's MMV function) yields the opposite result, the thus-predicted  $D - G(1)$ 's being *larger* than their true values. As a result, the fact that this estimate of the  $v=1$  binding energy is much closer to the present recommended  $2.6 (\pm 0.2) \text{ cm}^{-1}$  than to the  $3.7 \text{ cm}^{-1}$  of Tanaka *et al.* [4, 5], increases our confidence on the former.

## 2.2. The zero-point energy

One of our main disagreements with Maitland's [3] analysis concerns his method of estimating the zero-point energy,  $G(0)$ . To do this, he first followed

† In addition to the potentials described above and in [4], both the LJ (12, 6) potential which Koehler [7] obtained from solid-state data and the new generalized LJ potential of Maitland and Smith [8] have unacceptable  $\Delta G_{1/2}$  values of  $11.62$  and  $12.69 \text{ cm}^{-1}$ , respectively. It was previously shown [2] that the differential scattering cross sections predicted by the former are also unsatisfactory.

‡ The difference between this value and Maitland's [3]  $3.04 (\pm 0.41) \text{ cm}^{-1}$  is due to our use of Tanaka *et al.*'s [10] improved version of the method.

the example of [9] by fitting the experimental vibrational spacing to the near-dissociation expression

$$G(v) = D - [(v_D - v)H_6]^3, \quad (1)$$

where  $D$  is the dissociation energy,  $v_D$  the effective vibrational quantum number at dissociation, and  $H_6$  is a constant depending on the theoretically known van der Waals potential constant  $C_6$ . The values of both  $v_D = 2.292 (\pm 0.05)$  and the  $v = 1$  binding energy obtained in this way are quite reasonable. However, he then attempted to determine the 'potential-minimum' vibrational constants  $\omega_e$  and  $\omega_e x_e$  by fitting this binding energy and the experimental  $\Delta G_{1/2}$  value to the quadratic

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 \quad (2)$$

while assuming that the  $v_D$  value obtained from the *cubic* expression (1) still represented the dissociation limit. The invalidity of this approach is clearly illustrated by the fact that the derivative  $dG/dv$  obtained on substituting this  $\omega_e$  and  $\omega_e x_e$  into equation (2) goes to zero at  $v = 1.881$  rather than at  $v_D$ , and is equal to  $-4.04 \text{ cm}^{-1}$  at  $v_D$ ! Thus, it appears difficult to attach any significance to Maitland's [3]  $G(0)$  estimate of  $10.5 (\pm 1.0) \text{ cm}^{-1}$ .

This too-small  $G(0)$  value may also be the source of the discrepancies between the estimates of  $G(0) = 10.5 (\pm 0.5) \text{ cm}^{-1}$ ,  $\Delta G_{1/2} = 13.6 (\pm 0.3) \text{ cm}^{-1}$  and  $[D - G(1)] = 3.04 (\pm 0.7) \text{ cm}^{-1}$  which Maitland used in deriving his MMV function, and their actual values for this potential (see table 1). It would certainly lead to an RKR width versus depth function which is too broad at low energies, and the effect of the viscosity and virial coefficient data in attempting to correct this shape may be the source of these differences.

In determining a more reliable value for  $G(0)$  use of the near-dissociation expression equation (1) is inappropriate, since the analyses of the analogous states of  $\text{Ar}_2$  and  $\text{Kr}_2$  imply that it will give an upper bound to the true value. However, this upper bound of  $13.5 (\pm 0.5) \text{ cm}^{-1}$  would itself appear to rule out all but one (the present ESMSV) of the potentials considered in [4].

In accord with Tanaka *et al.* [4], we feel that reliable conventional anharmonicity constants cannot be determined for this case, and that the best estimate of  $G(0)$  will consist of a value computed from a reliable potential function determined from other properties. Thus, the recommended  $G(0)$  given in table 1 is based on the calculated values for the two MSV potentials.

### 3. CONCLUSIONS

The preceding discussion shows that even the limited spectroscopic data presently available for the bound levels of ground-state  $\text{Ne}_2$  effectively discriminate among the diverse potential functions proposed for this species. The two MSV potentials derived from solid-state data clearly have more realistic attractive wells than any other functions yet proposed. Unfortunately, even the spectroscopic data cannot as yet discriminate between them. However, they still yield significantly improved estimates of the molecular dissociation energy  $D_0$  and potential well depth  $D_e$  (see table 1).

It should be remembered, that these curves were derived from data which depend mainly on the potential well. While they also give satisfactory predictions of experimental second virial coefficients and differential scattering cross

sections [2], the short-range repulsive parts of these functions may require further improvements. This is suggested by the fact that they do not provide very accurate predictions of the isotopic thermal diffusion coefficient  $\alpha_T$ .

We are grateful to Professor R. A. Aziz for helpful discussions, and to Dr. G. C. Maitland for a number of useful criticisms.

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