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Spectroscopic Reassignment and Ground State
Dissociation Energy of Molecular Iodine

by

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ABSTRACT

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The discussion of the properties of the ground electronic state in section V of WIS-TCI-331 (12-27-68) concomitant with the present work is virtually unchanged. The only changes in substance consist of dropping the RKR turning points above $v'' = 82$, and slight adjustments to the constants in Eqs. (5) and (6).

I. Introduction

Verma observed[1] six series of UV resonance emission doublets which were excited by absorption of the 1830.4 Å iodine atomic line by molecules in 5 rotational levels of the $v'' = 0$ level[2] of the ground electronic state of I_2 . This absorption corresponded to transitions into 5 resonant vibrational-rotational levels of an excited 0_u^+ electronic state, and the subsequent emission from these levels yielded the observed series. Verma concluded[1] that this emission always produced molecules in the ground electronic state, and this is unquestionably true for those final states to which he assigned vibrational quantum numbers $v'' \leq 84$. However, the separate set of levels at the convergence limit of the emission spectrum (Verma's $v'' = 98$ to 115) causes a strange flattening of the Birge-Sponer plot for the ground state. Furthermore, their sharp convergence limit cut-off lies above a value of the ground state dissociation energy obtained from other data, which implies that the state to which they belong has a potential maximum. This suggests that the present best value of the dissociation energy,[1] which is based on the position of this cut-off, is too large by an amount equal to the height of the barrier. The present paper presents a new value of the ground state dissociation energy, and proposes that the levels in question be reassigned to the $0_g^+(^3\Pi)$ state.

II. Dissociation Energy of Ground State $I_2(X\ 0_g^+(^1\Sigma))$

Two main approaches to the determination of the dissociation energy are considered. In the first, an estimate for D_o is obtained by

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II. Dissociation Energy of Ground State $I_2(X\ 0_g^+(^1\Sigma))$

Two main approaches to the determination of the dissociation energy are considered. In the first, an estimate for D_o is obtained by subtracting the $^2P_{3/2}$ - $^2P_{1/2}$ spin-orbit splitting of iodine atoms[3] from the convergence limit of the $B\ 0_u^+(^3\Pi)$ - $X\ 0_g^+(^1\Sigma)$ band spectrum.

Steinfeld, Campbell, and Weiss[4] recently remeasured the energies of a number of levels of the $B\ 0_u^+(^3\Pi)$ state, up to $v' = 51$. Much earlier, Brown had reported band head measurements for levels $v' = 48$ to 72.[5] Although his absolute energies are approximately 12.1(±2.3) cm^{-1} higher than the overlapping ($v' = 48$ to 51) values of Steinfeld et al.,[4] Brown's relative spacings should be fairly good. Combining the corrected (by subtracting 12.1(±2.3) cm^{-1}) $v' = 72$ energy with a short 19.5(±2) cm^{-1} extrapolation[7,8] places the B state dissociation limit some 20032(±4) cm^{-1} above the $v'' = 0$, $J'' = 0$ level of the ground state. Subtracting from this the 7603.15 cm^{-1} $^2P_{1/2}$- $^2P_{3/2}$ spin-orbit splitting energy[9] yields $D_o = 12429(\pm 4)$ cm^{-1}.[10] This result corresponds to the B state having 89(±1) vibrational levels.[8]

A second approach to D_o, that used by Verma,[1] is based on the sharp low energy cut-off of the UV resonance series at the convergence limit. The electronic assignment of the lower state of this series is immaterial, since it could only dissociate to yield two ground state $^2P_{3/2}$ atoms. Furthermore, the original rotational assignment of this resonance series ($J_r = 25$) is based on the rotational constants for the emitting levels, and hence is valid independent of the electronic assignment of the final state. Utilizing the data in essentially the same manner as Verma[1] yields a D_o estimate of 12452.4(±1.8) cm^{-1}.[11]

In general, the final electronic states of the two transitions considered above may have repulsive potential barriers as well as attractive wells. Therefore, the two estimates of D_o are both upper bounds, being equal to the true D_o plus the height of the appropriate barrier.

Since the first value obtained is 24($\pm$6) cm^{-1} smaller than the second, the state giving rise to the latter must have a rotationless (J = 0) potential barrier at least 24($\pm$6) cm^{-1} high.

The moderately long-range interaction of two ^2P ($^2P_{3/2}$ or $^2P_{1/2}$) iodine atoms may be expressed as[13]

$$V(R) = C_5/R^5 + C_6/R^6 + C_8/R^8 + C_{10}/R^{10} + \ldots \qquad (1)$$

where the first term arises from the first order perturbation energy, and the next three terms from the second order. It may readily be shown that C_6, C_8, and C_{10} are negative (attractive) for all molecular states formed from two ground state ($^2P_{3/2}$) atoms.[14] Furthermore, theoretical values of C_5 have been calculated for all the states formed on combining $^2P_{3/2}$+ $^2P_{3/2}$ or $^2P_{3/2}$+ $^2P_{1/2}$ atoms.[13,15] These values show which states are attractive and which are repulsive at the large distances at which the R^{-5} term dominates the interaction.

The theoretical C_5 for the B $0_u^+(^3\Pi)$ state, which dissociates to $^2P_{3/2}$+ $^2P_{1/2}$, is negative (attractive).[13] Furthermore, in reference 8 it is shown that the potential at the outer turning points of the highest observed B state levels is dominated by this R^{-5} term. Therefore, the B $0_u^+(^3\Pi)$ potential cannot have a barrier maximum, D_o = 12429($\pm$4) cm^{-1} for the ground electronic state, and the state giving rise to the UV convergence limit resonance series must have a potential barrier <u>ca</u>. 24($\pm$6) cm^{-1} high.

The above D_o value is based on the observed convergence of $B\ 0_u^+(^3\Pi)$ vibrational levels to their dissociation limit. However, it is also confirmed from consideration of the highest observed $X\ 0_g^+(^1\Sigma)$ levels. In reference 8, an expression is given for the vibrational energies of levels lying close to the top of a potential well where the curvature of the Birge-Sponer plot is positive. This positive curvature is exhibited by ground state I_2 levels lying above $v'' = 73$; however, vibrational levels have been observed only up to $v'' = 84$,[1] and the energies of the two levels above $v'' = 82$ are somewhat uncertain.[12] When the smoothed energies of levels $v'' = 77$ to 82[12] were fitted to the expression given in reference 8, the value $D_o = 12426(\pm 20)\ \mathrm{cm}^{-1}$ was obtained. The relatively large uncertainty is to be expected, in view of the fact that $v'' = 82$ lies $496\ \mathrm{cm}^{-1}$ below the dissociation limit. This result independently confirms the above value of $D_o = 12429(\pm 4)\ \mathrm{cm}^{-1}$; furthermore, it suggests that the convergence limit resonance series (converging to $12452.4(\pm 1.8)\ \mathrm{cm}^{-1}$) cannot correspond to the ground electronic state.

III. Reassignment of the UV Resonance Series at the Convergence Limit

A. The Need for a Reassignment

The data considered for reassignment are the lines in the convergence limit portion of Verma's resonance series IVb, presented in his Table V.[1] He concluded that the lower state of this series was the ground electronic state. While this is unquestionably the case for the other five UV resonance series observed, it is shown below that this assignment is quite implausible for the series in question.

The theoretical C_5 for the ground $X\ 0_g^+(^1\Sigma)$ state of I_2 is zero;[13,15] hence, the moderately long-range forces are dominated by the attractive second order perturbation terms (C_6, C_8, and C_{10}). Since the exchange forces are also attractive (as is evidenced by the deep potential well), this state cannot have a potential maximum. Therefore, the final state of the UV convergence limit resonance series cannot be the ground state. This confirms the results of the fit to the highest observed ground state levels, discussed at the end of section II.

A more qualitative objection to the original assignment is based on the Franck-Condon accessibility of the final levels. Verma's Fig. 1b,[1] shows that the emission into the eighteen adjacent levels at the dissociation limit has roughly constant intensity. Therefore, it seems strange that none of the 23 levels immediately below his $v'' = 98$ are sufficiently accessible from the upper state to allow measurable emission. The observed behavior suggests that Verma's $v'' = 98$ is the lowest vibrational level of some excited electronic state.

A final argument against the $X\ 0_g^+(^1\Sigma)$ assignment is based on the expected behavior of a Birge-Sponer plot for vibrational levels lying near the dissociation limit. It has been shown that when the outer branch of the potential in this region is a short sum of attractive inverse power terms, the plot should have positive (upward) curvature.[8,16] For the ground state of I_2 this positive curvature is observed above $v'' = 73$ and increases from there up to $v'' = 82$ (the highest well known level below the convergence limit resonance series) where it equals 0.060 cm^{-1}.[12] For this state, the theory suggests[8] that above the point of inflection at $v'' = 73$ the curvature $(d^3G(v)/dv^3)$ should increase, perhaps pass through a slight maximum, and asymptotically approach a constant value of $94./\sqrt[4]{C_6}$ cm^{-1} (where C_6 is in cm^{-1} $\mathrm{\AA}^6$).[17] For a reasonable C_6 of $3.0 \times 10^{+6}$ cm^{-1} $\mathrm{\AA}^6$, this asymptotic curvature would be 0.054 cm^{-1}. On the other hand, the level spacings in the convergence limit resonance series show negligible curvature ($\lesssim 0.001$ cm^{-1}; see Figure 2).[18] This strengthens the argument that these levels cannot belong to the ground state.

Theory shows[8] that vibrational levels lying near the dissociation limit which yield a linear Birge-Sponer plot, correspond to a long-range potential which is either exponential, or is dominated by an effective inverse power term R^{-n} with n being large ($n \gg 10$).[19] This high effective power is qualitatively the type of behavior one would expect on the attractive branch of a potential barrier arising from a sum of attractive and repulsive inverse power terms.

B. The Reassignment

The final state to which the levels in question belong must have a potential barrier of height ca 24($\pm$6) cm^{-1} as well as an attractive well, and must correlate with two ground state $^2P_{3/2}$ atoms. Nine states in addition to the ground state correlate with two ground state atoms; of these three are non-degenerate and six are doubly Ω-degenerate.[20] The nature of the emission and absorption spectrum of Verma's upper state clearly indicates that it is 0_u^+;[21] therefore, the $\Delta\Omega = 0, \pm 1$ electronic selection rule immediately removes two possible assignments. In addition, the gerade-ungerade symmetry selection rule for electric dipole[23] transitions, ($g \leftrightarrow u$, $g \not\leftrightarrow g$, $u \not\leftrightarrow u$)[24] leaves the $0_g^+(^3\Pi)$ and the $1g(^3\Pi)$ states as the only electronically allowed assignments.

The rotational selection rules for transitions from a 0_u^+ state into singly degenerate 0_g^+ or doubly Ω-degenerate $1g$ states allow $\Delta J = \pm 1$ and $\Delta J = 0, \pm 1$ transitions respectively, the first giving rise to doublet and the second to triplet structure. While transitions into the separate branches of the Ω-doublet ($1g$) would correspond to $\Delta J = \pm 1$ and $\Delta J = 0$ respectively, the intensity of the Q-branch ($\Delta J = 0$) is theoretically twice that of the P or R branches, so this spectrum would be observed as either the full triplet or as a singlet.[24] Verma was able to resolve the structure of the emission into the three lowest levels of the convergence limit series, and it is clearly doublet in nature. Therefore, the only completely allowed reassignment of the levels in question is to the $0_g^+(^3\Pi)$ state.

The theoretical long-range R^{-5} term for the $0_g^+(^3\Pi)$ state is repulsive[13,15] while its R^{-6}, R^{-8}, and R^{-10} terms are attractive;[14] thus it seems plausible that it will have an attractive well bounded by a potential maximum. On the other hand, the theoretical C_5 for this state (2.3×10^5 cm^{-1} Å^5)[13,15] is too small to yield a $24(\pm 6)$ cm^{-1} barrier, either alone or when the competing attracitve R^{-6} term is taken into account.[25]

Although the origin of the potential barrier is somewhat uncertain, the reassignment of the UV convergence limit resonance series to the $0_g^+(^3\Pi)$ state still seems much more likely than its original assignment as X $0_g^+(^1\Sigma)$. The validity of this reassignment will now be assumed and the concomitant properties of the $0_g^+(^3\Pi)$ state will be considered.

IV. The $0_g^+(^3\Pi)$ State

This state was previously observed by Venkateswarlu[22] in diffuse bands arising as emission from discrete levels of the previously mentioned highly excited 0_u^+ state, into the $0_g^+(^3\Pi)$ continuum. Venkateswarlu concluded that its potential was repulsive in the neighborhood of the mimimum of the ground state potential, and that it lay below and to the left of the B $0_u^+(^3\Pi)$ curve.[22] This same conclusion was also inferred by Steinfeld from considerations involving the quenching of B state fluorescence.[26]

Due to this intermediate-range repulsiveness of the $0_g^+(^3\Pi)$ curve, its potential mimimum must lie at reasonably large R and the well is unlikely to be very deep. The non-crossing rule which forbids it from crossing the ground state X $0_g^+(^1\Sigma)$ curve also implies that the well must be quite shallow. In view of this, and of the roughly constant intensity of the emission into the observed levels, it seems probable that the lowest observed level is $v' = 0$. If this numbering is incorrect, it is unlikely to be more than one or two units too small.

The energies and assumed vibrational assignments of the convergence limit levels are given in Table I. The small rotational energy contributions to the observed lines were removed after extrapolating beyond the three experimental $B_{v'}$ values in the manner shown in Figure 1. Utilizing Figure 1 rather than the approach of reference 1 places the convergence limit of this series at 12454.0(±0.3) cm^{-1} (1.6 cm^{-1} higher than the previous estimate). This yields 25(±5) cm^{-1} as a better estimate of the height of the potential maximum. Nine of the eighteen observed levels are metastable (for $J' = 0$), being bound only by this potential barrier.

Table I: $I_2(0_g^+(^3\Pi))$ Vibrational Energies (in cm^{-1})
Expressed Relative to the $v'' = 0$, $J'' = 0$ Level of the Ground State.

v'	E	v'	E	v'	E
0	12362.4	6	12413.6	12	12444.0
1	12372.5	7	12420.1	13	12447.2
2	12381.9	8	12426.0	14	12449.7
3	12390.5	9	12431.4	15	12451.5
4	12399.0	10	12436.1	16	12452.9
5	12406.6	11	12440.4	17	12453.7

Using the above vibrational assignment, the vibrational energies may be represented within a standard error of ±0.08 cm^{-1} by:

$$E(v') = 12357.3 + 10.522(v' + \tfrac{1}{2}) - 0.2866(v' + \tfrac{1}{2})^2 \qquad (2)$$

where the energy zero is the $v'' = 0$, $J'' = 0$ level of the ground state. This shows that this state has a potential well at least 72(±4) cm^{-1}

deep (relative to the dissociation limit, not the potential maximum). Furthermore, the observed rotational splittings would place the potential minimum at 6.0($\pm$0.6) Å. The experimental vibrational spacings are compared with those calculated from expression (2) in Figure 2; the curve suggests that there may exist one more, as yet unobserved, quasibound state.

The potential curve for $0_g^+(^3\Pi)$ is shown schematically in Figure 3, together with curves for a number of neighboring states. The ground state potential up to 11933 cm^{-1} and the B $0_u^+(^3\Pi)$ state potential up to 19703 cm^{-1} are RKR potentials (taken from reference 12, and references 4 and 6 respectively). The $0_u^-(^3\Sigma)$ curve was taken from reference 27 and the A $1u(^3\Pi)$ curve is based on the conclusions of Brown.[28] At large distances the A $1u(^3\Pi)$ and X $0_g^+(^1\Sigma)$ curves must cross, since the latter dies off as R^{-6}, and the former as R^{-5}. Furthermore, the A $1u(^3\Pi)$ curve may also cut across the $0_g^+(^3\Pi)$ well. The theoretical C_5 for $0_u^-(^3\Sigma)$ is 1/3 larger than that for $0_g^+(^3\Pi)$,[13,15] so these curves should not cross at long range.

V. Conclusions

It has been shown that contrary to the original assignment, a portion of the UV resonance spectrum of I_2 does not correspond to emission into the ground electronic state. The most probable reassignment for the levels in question was found to be $0_g^+(^3\Pi)$. This state appears to be an example of a van der Waals[29] molecule, bound only by the moderately long range dispersion forces,[30] which has a potential barrier.

If the present reassignment is correct, Verma's UV spectrum[1] is the first observation of the discrete levels of the $0_g^+(^3\Pi)$ state. These levels clearly cannot be observed in absorption from the ground state because of the $g \nleftrightarrow g$ symmetry selection rule. However, they may be observable in near IR fluorescence (at around 1.4 microns) from some of the higher levels of the B $0_u^+(^3\Pi)$ state. One restriction to this type of measurement is that the fluorescencing state cannot have a very high rotational quantum number, as in this case the centrifugal potential would bury the shallow $0_g^+(^3\Pi)$ well. However, if appropriate B $0_u^+(^3\Pi)$ levels can be excited, these $0_g^+(^3\Pi)$ levels may be observed together with neighboring X $0_g^+(^1\Sigma)$ levels, giving direct confirmation of the proposed reassignment.

VI. Acknowledgments

I am pleased to acknowledge helpful discussions with Professor A. S. Dickinson, the comments, encouragement, and support of Professor R. B. Bernstein, and interesting correspondence with Professor J. I. Steinfeld. I am also deeply indebted to Professor R. D. Verma for some very telling criticisms of an early version of this paper.

Footnotes

1. R. D. Verma, J. Chem. Phys. 32, 738 (1960).
2. Throughout, double primed quantities will refer to the ground electronic state and single primed quantities to an excited electronic state.
3. This step is necessary because B $0_u^+(^3\Pi)$ dissociates to $^2P_{3/2}+{}^2P_{1/2}$, while the ground state dissociates to $^2P_{3/2}+{}^2P_{3/2}$.
4. J. I. Steinfeld, J. D. Campbell, and N. A. Weiss, J. Mol. Spectry. 29, 204 (1969).
5. W. G. Brown, Phys. Rev. 38, 709 (1931). The accepted vibrational numbering for the B state has recently been revised,[6] so the numbering used by Brown should be decreased by one.
6. J. I. Steinfeld, R. N. Zare, L. Jones, M. Lesk, and W. Klemperer, J. Chem. Phys. 42, 25 (1965).
7. The extrapolation procedure is based on a new method for determining long range forces from vibrational spacings, which is reported elsewhere.[8]
8. R. J. LeRoy and R. B. Bernstein, to be published. The extrapolation to the dissociation limit of the B state is discussed here in more detail.
9. C. Moore, U. S. Nat. Bur. Std. Circ. No. 467, 3, 105 (1958). The results quoted are based on the data of C. C. Kiess and C. H. Corliss (U. S. Nat. Bur. Std. J. Res. 63A, 1 (1959)).
10. This value differs from Brown's[5] 12439 cm^{-1} mainly because of the apparent 12.1 cm^{-1} error in his absolute energies, and because he used a somewhat less accurate value (7598 cm^{-1}) of the spin-orbit

splitting energy. However, this effect is somewhat ameliorated by the present improved extrapolation to the dissociation limit.[7,8]

11. The slight difference with Verma's[1] 12452.5(±1.5) cm^{-1} arises from the use of a slightly different frequency for the line exciting the resonance series (see reference 12), and the use of the $J = 26$ rotational energy rather than $J = 24$.

12. R. J. LeRoy, following paper.

13. T. Y. Chang, Rev. Mod. Phys. 39, 911 (1967).

14. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons Inc., 1954). The expression for the second order perturbation energy derived in section 13.3b is negative for all states formed from two ground state atoms.

15. J. K. Knipp, Phys. Rev. 53, 734 (1938).

16. This was noted previously by H. Harrison and R. B. Bernstein (J. Chem. Phys. 38, 2135 (1963)) for the cases of Lennard-Jones (12,6) and exponential (α,6) potentials, both of which have R^{-6} tails.

17. This is true because the long-range potential for the ground state is described by expression (1) with $C_5 = 0.0$[13,15] and C_6, C_8, and C_{10} all attractive (negative).[14]

18. A third-order least-squares fit to these energies (see Table I) had the same standard error as a second order fit (0.08 cm^{-1}), and yielded a curvature of only 0.0012 cm^{-1}. A curvature rate of 0.054 cm^{-1} over the 18 observed levels would add 7.8 cm^{-1} to the dG/dv ($\Delta G(v)$) for the highest observed level, over the value

obtained by linearly extrapolating from the lowest dG/dv values. For a curvature of 0.0012 cm^{-1}, this effect is reduced to 0.17 cm^{-1}.

19. The potential is assumed to be fitted to an expression of the form $A/R^n + B$ where $n = -(1 + d \log(dV/dR)/d \log R)$.

20. R. S. Mulliken, Phys. Rev. <u>36</u>, 699 (1930).

21. This upper state has been previously observed in absorption by H. Cordes, (Z. Physik <u>97</u>, 603 (1935)), and in emission by P. Venkateswarlu.[22] This electronic assignment was not questioned in the later analyses by L. Mathieson and A. L. G. Rees (J. Chem. Phys. <u>25</u>, 753, 1956) and by A. Nobs and K. Wieland (Helv. Phys. Acta <u>39</u>, 564, 1966).

22. P. Venkateswarlu, Proc. Ind. Acad. Sci. <u>24A</u>, 480 (1946). The author would like to thank R. D. Verma for bringing this reference to his attemtion.

23. The intensity of the observed emission indicates that the transitions could only be electric diple.

24. G. Herzberg, Spectra of Diatomic Molecules, second edition (d. Van Nostrand Co. Inc., Toronto, Canada, 1950).

25. F. E. Cummings has developed a new method of calculating R^{-6} terms and applied it to the different states of I_2 correlating with two ground state atoms. This work is to be presented at the 24th Symposium on Molecular Structure and Spectroscopy in Columbus, Ohio, in September, 1969; the present author is grateful to Dr. Cummings for making his results available in advance.

26. J. I. Steinfeld, private communication (1969).

27. E. O. Degenkolb, J. I. Steinfeld, E. Wasserman, and W. Klemperer, to be published.

28. W. G. Brown, Phys. Rev. 38, 1187 (1931).

29. See reference 24, p. 377.

30. This seems rather likely since the $0_g^+(^3\Pi)$ potential well is quite shallow and its $R_{EQ} \approx 6$ Å, is considerably larger than the 2.66 Å for the ground X $0_g^+(^1\Sigma)$ state,[12] 3.03 Å for the B $0_u^+(^3\Pi)$ state[4] and *ca* 3.2 Å for the A $1u(^3\Pi)$ state.[28]

Legends for Figures

Figure 1. Rotational Constants for Final State of Convergence Limit Resonance Series

The v" numbering corresponds to Verma's $X\ 0_g^+(^1\Sigma)$ assignment[1] and v' numbering to the present $0_g^+(^3\Pi)$ assignment. • are Verma's experimental values and the arrow denotes the highest observed level.

Figure 2. Vibrational Spacings of Levels in Convergence Limit Resonance Series

v" represents the old $X\ 0_g^+(^1\Sigma)$ vibrational numbering[1] and v' the proposed $0_g^+(^3\Pi)$ numbering. The curve is generated from expression (2).

Figure 3. Schematic Potential Curves for $0_g^+(^3\Pi)$ and Some Neighboring States

The zero of energy is the v" = 0, J" = 0 level of the ground electronic state.

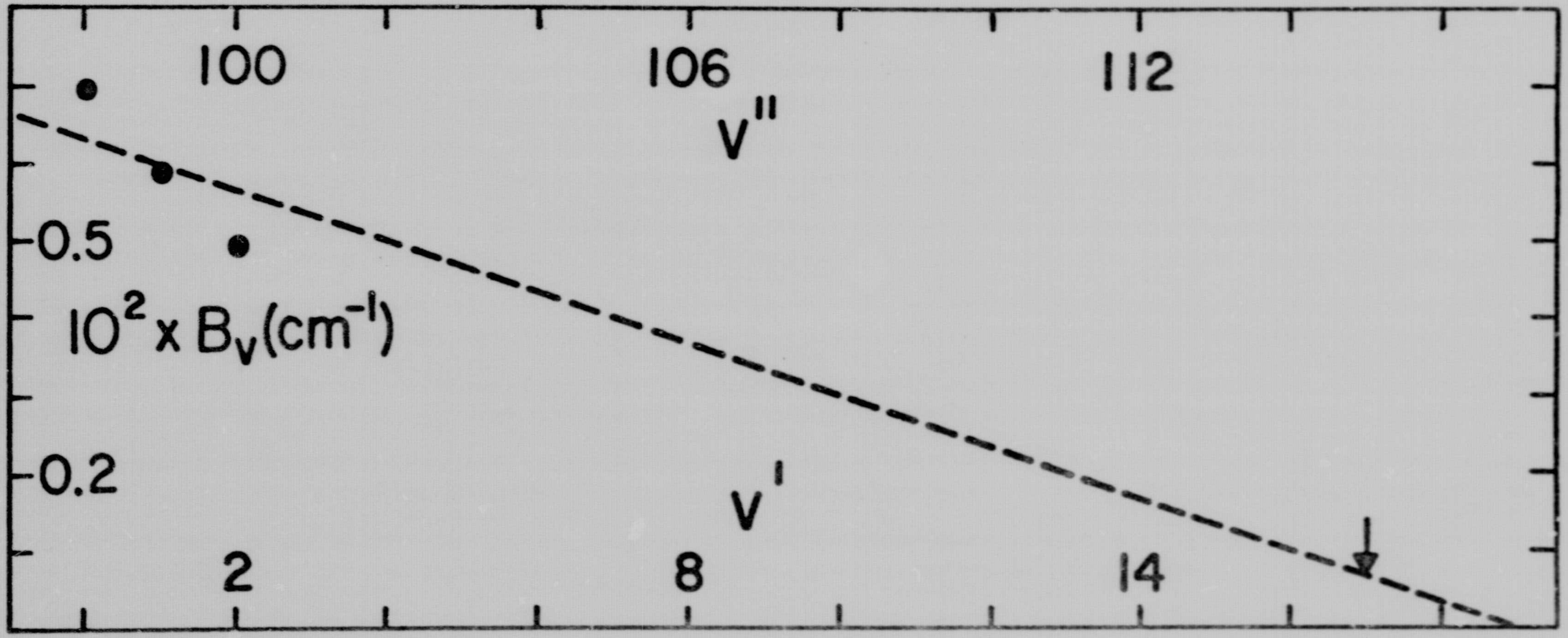

Figure 1

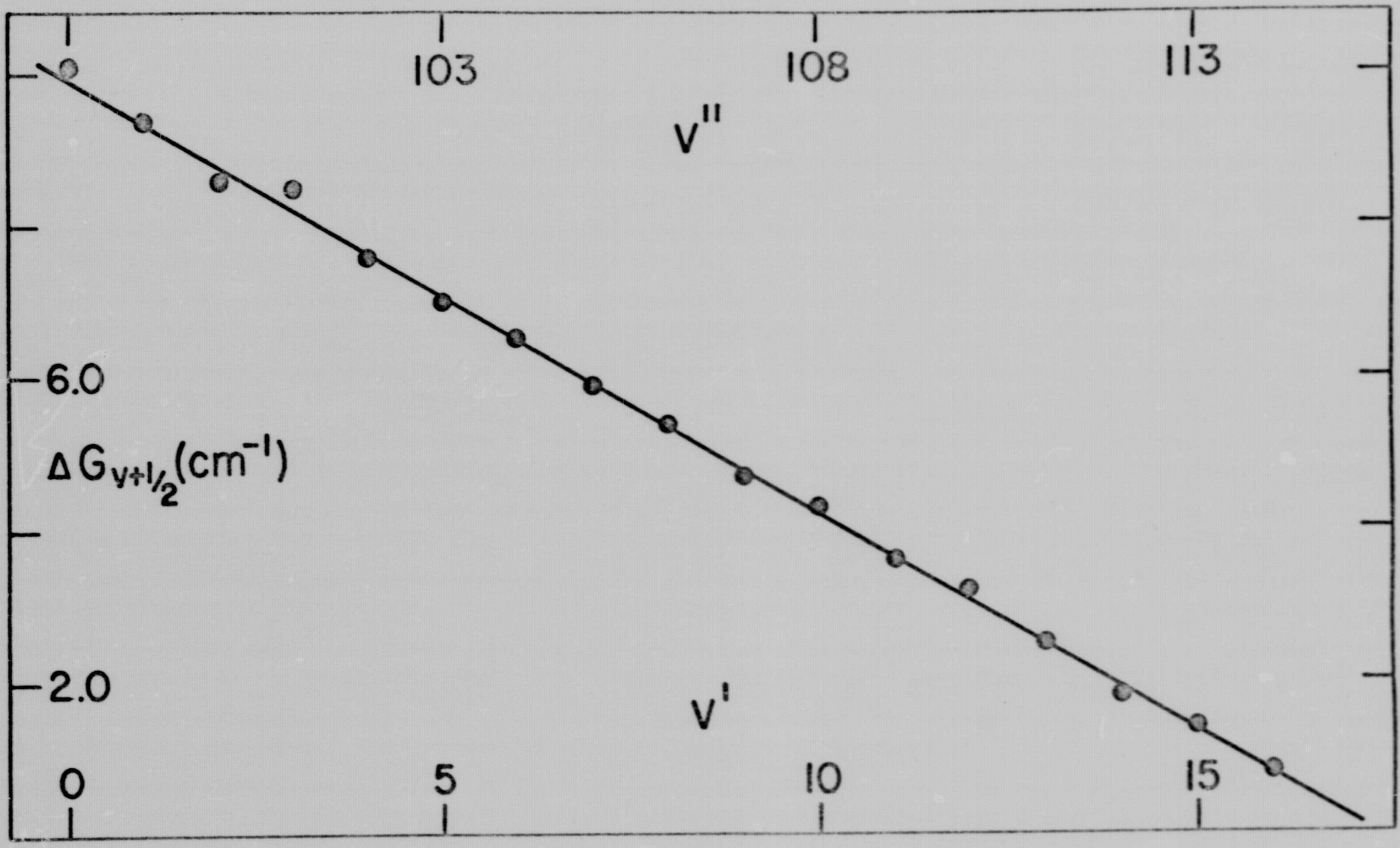

Figure 2

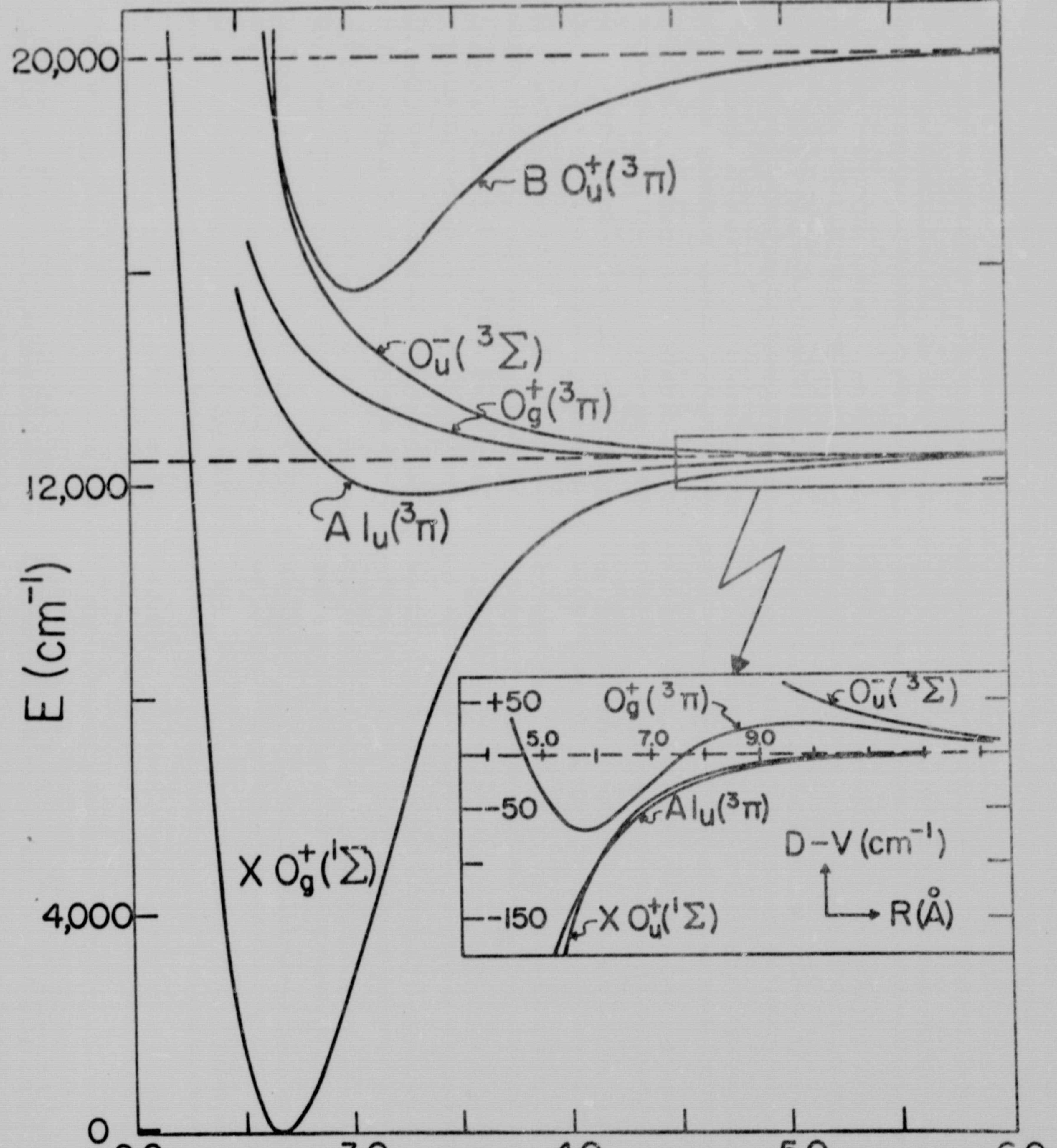
20,000
12,000
4,000
0
2.0
3.0
4.0
5.0
6.0
R (Å)
E (cm^{-1})
B $0_u^+(^3\Pi)$
$0_u^-(^3\Sigma)$
$0_g^+(^3\Pi)$
A $1_u(^3\Pi)$
X $0_g^+(^1\Sigma)$
+50
-50
-150
5.0
7.0
9.0
$0_g^+(^3\Pi)$
$0_u^-(^3\Sigma)$
A $1_u(^3\Pi)$
X $0_u^+(^1\Sigma)$
D−V (cm^{-1})
R(Å)

Figure 3