# SHORT COMMUNICATIONS

## ON THE CANCELLATION OF CERTAIN THREE- AND FOUR-BODY INTERACTIONS IN INERT GASES

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[Manuscript received 10 March 1972]

Recently two of us[1] showed that inclusion of three-body dipole–quadrupole interactions as well as three-body dipole interactions led to substantial improvement in agreement with experiment for third virial coefficients of argon, computed using the pair potential of Barker and Pompe.[2] It was also shown that these three-body dipole–quadrupole interactions make a non-negligible contribution to the energy of crystalline argon. The purpose of this note is to point out that there is substantial cancellation in crystalline inert-gas elements between the *three*-body dipole–quadrupole energy and the *four*-body triple-dipole energy which has recently been evaluated by Doran and Zucker.[3] This is shown in Table 1 which lists the estimates of Johnson and Spurling[1] and Doran and Zucker[3] for these quantities. There is considerable uncertainty in the dipole–quadrupole terms, first because they are based on relatively crude approximate expressions involving quadrupole polarizabilities due to Bell,[4] and secondly because the quadrupole polarizabilities themselves are derived from quantum mechanical calculations which may not give higher accuracy. The bracketed

Table 1

MANY-BODY DIPOLE (D) AND QUADRUPOLE (Q) CONTRIBUTIONS TO ENERGY OF CRYSTALLINE INERT-GAS ELEMENTS

All values are in J mol$^{-1}$

| Inert-gas element | Ref. | Cohesive energy | $E(\mathrm{DDD})_3$ | $E(\mathrm{DDQ})_3$ | $E(\mathrm{QQD})_3$ | $E(\mathrm{QQQ})_3$ | $E(\mathrm{DDD})_4$ |
|---|---|---|---|---|---|---|---|
| Ne | 3 | −1876 | 62·4 | 14·3 | 2·3 | 0·2 | −4·8 |
| | | | | (15·5) | (2·7) | (0·2) | |
| Ar | 3 | −7746 | 579·6 | 120·6 | 17·8 | 1·2 | −126·7 |
| | 3 | | | (173·8) | (37·0) | (3·5) | |
| | 4 | | 577·0 | 173·6 | 41·4 | 3·5 | |
| Kr | 3 | −12212 | 1004·0 | 220·1 | 34·3 | 2·4 | −281·4 |
| Xe | 3 | −15818 | 1597·9 | 373·6 | 62·0 | 4·6 | −636·6 |

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[1] Johnson, C. H. J., and Spurling, T. H., *Aust. J. Chem.*, 1971, **24**, 2205.
[2] Barker, J. A., and Pompe, A., *Aust. J. Chem.*, 1968, **21**, 1683.
[3] Doran, M. B., and Zucker, I. J., *J. Phys.* (*C*), 1971, **4**, 307.
[4] Bell, R. J., *J. Phys.* (*B*), 1970, **3**, 751.

estimates of Doran and Zucker[3] are based on the computed quadrupole polarizabilities of Lahiri and Mukherji;[5] they agree very well with the estimates of Johnson and Spurling,[1] which rest on the same quadrupole polarizability. The unbracketed estimates of Doran and Zucker[3] are based on quadrupole polarizabilities of Feiock and Johnson.[6] These values are probably less accurate, but the differences between the two sets give a reasonable estimate of the uncertainty.

For argon it will be seen that the sum of the dipole–quadrupole three-body interactions and the four-body triple-dipole interactions comes out as 13, 88, or 92 J $mol^{-1}$, according to which estimate of the polarizability is adopted. Even the higher value is only about 15% of the triple-dipole contribution, and only about twice as large as the experimental error in the cohesive energy of solid argon. In view of the uncertainty, it appears to be a reasonable approximation at present to neglect the sum of the three-body dipole–quadrupole and the four-body triple-dipole interactions in condensed argon. Some weight is added to this conclusion by the fact that successive refinements of the pair potential based on this assumption[7] led to a potential in excellent agreement with the molecular beam differential scattering data of Parson, Siska, and Lee.[8] The additional three-body interaction which leads to excellent agreement with experimental third virial coefficients is to a considerable extent cancelled in crystalline argon by the four-body term.

A similar, and perhaps even more complete, cancellation appears to occur in the case of krypton. For neon the net contribution is positive and for xenon it is negative, though still small relative to the triple-dipole contribution.

[5] Lahiri, J., and Mukherji, A., *J. phys. Soc. Japan*, 1966, **21**, 1178; *Phys. Rev.*, 1966, **141**, 428; 1967, **153**, 386; 1967, **155**, 24.

[6] Feiock, F. D., and Johnson, W. R., *Phys. Rev.*, 1969, **187**, 139.

[7] Barker, J. A., Fisher, R. A., and Watts, R. O., *Molec. Phys.*, 1971, **21**, 657.

[8] Parson, J. M., Siska, P. E., and Lee, Y. T., *J. chem. Phys.*, 1972, **56**, 1511.