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Rotational spectroscopy of $H_3P\cdots BrCl$ and the systematics of intermolecular electron transfer in the series $B\cdots BrCl$, where $B{=}CO$, HCN, H_2O, C_2H_2, C_2H_4, H_2S, NH_3, and PH_3

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Ground-state rotational spectra of the isotopomers $H_3P\cdots{}^{79}Br^{35}Cl$, $H_3P\cdots{}^{81}Br^{35}Cl$, $H_3P\cdots{}^{79}Br^{37}Cl$, $H_3P\cdots{}^{81}Br^{37}Cl$, $D_3P\cdots{}^{79}Br^{35}Cl$, and $D_3P\cdots{}^{81}Br^{35}Cl$, of the phosphine–bromine monochloride complex were observed by the pulsed-jet, Fourier-transform method, incorporating a mixing nozzle to preclude reaction among the component gases. Each isotopomer exhibited a symmetric-top-type spectrum which yielded accurate values of the spectroscopic constants B_0, D_J, D_{JK}, χ_{aa}(Br), χ_{aa}(Cl), M_{aa}(Br), and M_{bb}(Br) on analysis. Interpretations of the changes in the B_0 values with isotopomer showed that the intermolecular bond involves P and Br, with $r(P\cdots Br)=2.869(1)$ Å and that the BrCl bond increases in length by ~0.04 Å on complex formation. Changes in the halogen nuclear quadrupole coupling constants when $H_3P\cdots BrCl$ is formed lead, with the aid of the Townes–Dailey model, to the conclusion that a fraction $\delta_i=0.100(5)$ of an electron is transferred from P to Br on complex formation, while the polarization of BrCl by PH_3 can be viewed as the transfer of $0.128(2)e$ from Br to Cl, leading to a net change of $-0.028(5)e$ in the population of the $4p_z$ orbital of Br. The complex is only of moderate strength, with an intermolecular stretching force constant $k_\sigma=11.5\,\mathrm{Nm}^{-1}$. Values of δ_i, similarly determined, for the series $B\cdots BrCl$, where $B{=}CO$, HCN, H_2O, C_2H_2, C_2H_4, H_2S, NH_3, or PH_3, are presented. It is shown that the variation of δ_i with the ionization energy I_B of the Lewis base B can be described by an expression $\delta_i=A\times\exp(-bI_B)$. This behavior is compared with that for the corresponding series $B\cdots ICl$. [S0021-9606(00)01037-0]

I. INTRODUCTION

The spectroscopy of complexes formed between halogen molecules and either rare gas atoms or Lewis base molecules is an area of significant activity.[1–6] The investigation of such complexes in the microwave region was pioneered by Klemperer and co-workers.[4–6] We have recently made a study of several extended series of complexes $B\cdots XY$, where B is a Lewis base and XY is either a homo- or heteronuclear dihalogen molecule, with the aim of identifying some generalizations about the interaction, and of understanding its detailed nature. In particular, we have developed a method[7] for determining the extent of both the inter- and the intramolecular electron transfer that accompanies formation of complexes. The method involves an interpretation of the changes in the X and Y halogen nuclear quadrupole coupling constants of XY when it is incorporated into the complex and is based on the Townes–Dailey model.[8,9] When applied to the series $B\cdots ICl$, where $B{=}Ar$, N_2, CO, HCN, H_2O, C_2H_2, C_2H_4, H_2S, NH_3, and PH_3, this approach leads to the fraction δ_i of an electron transferred from the electron-donor region *Z* of B to I, as well as to the fraction δ_p^{Cl} of an electron transferred from I to Cl. Some systematic behavior of δ_i and δ_p^{Cl} along the series was noted.[10] In particular, it was discovered that δ_i increases exponentially as the first ionization energy I_B of B decreases along the series. In fact, values of δ_i can be satisfactorily reproduced[10,11] by means of the expression

$$\delta_i=A\exp(-bI_B), \tag{1}$$

when the constants take the values $A=128.5$ and $b=0.734\,(\mathrm{eV})^{-1}$.

This result for the series $B\cdots ICl$ immediately poses several questions about other series $B\cdots XY$ that we have been investigating systematically.[12] For example, can the method for determining both δ_i and δ_p^Y be applied successfully to other $B\cdots XY$? When I in ICl is replaced by Br to give BrCl, how does δ_i change for a given B? Does δ_i in the series $B\cdots BrCl$ vary systematically with I_B and, in particular, does an expression of the type shown in Eq. (1) still describe the variation of δ_i with I_B?

A key member of the series $B\cdots ICl$ in connection with establishing the validity of Eq. (1) was that with $B{=}PH_3$, for PH_3 has the lowest value of I_B of all the Lewis bases employed[13] and accordingly the largest value of δ_i.[11] Although several members of the series $B\cdots BrCl$ have already been investigated by means of their rotational spectra and thereby their Br and Cl nuclear quadrupole coupling constants are available for determining δ_i, the complex $H_3P\cdots BrCl$ is not among them. Accordingly, we report here the identification of the rotational spectrum of $H_3P\cdots BrCl$, as observed by the pulsed-jet Fourier-transform microwave technique modified to incorporate a fast-mixing nozzle. In-

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terpretation of the ground-state spectroscopic constants of six isotopomers of $H_3P\cdots BrCl$ provides information about not only the angular and radial geometry of this complex but also the values of δ_i and δ_p^{Cl}. The answers to several of the questions posed in the preceding paragraph thereby become available.

II. EXPERIMENT

Ground-state rotational spectra of six isotopomers of the complex $H_3P\cdots BrCl$ were observed and measured by using a pulsed-jet, Fourier-transform microwave spectrometer. Details of this spectrometer, which is based on the design originally described by Balle and Flygare,[14] are available elsewhere.[15] BrCl was produced by mixing Br_2 (Aldrich) and Cl_2 (Aldrich) in equimolar amounts in the gas phase in a stainless steel stagnation tank at room temperature. The equilibrium constant for the reaction $Cl_2(g)+Br_2(g)=2BrCl(g)$ is $K_p^{\Theta}\approx 5$ at room temperature.[16] Because phosphine reacts with each of the components of the halogen mixture, it was not possible to premix PH_3, Br_2, and Cl_2 in the stagnation tank in the usual way. Possible reactions were precluded by using a fast-mixing nozzle,[17] which keeps the phosphine and the halogen mixture separate until the point at which both gases expand into the evacuated Fabry-Pérot cavity of the spectrometer.

The $Cl_2/Br_2/BrCl$ mixture was flowed continuously into the cavity through the central glass capillary (0.3 mm internal diameter) of the mixing nozzle at a rate sufficient to give a background pressure of $\sim 2\times 10^{-4}$ mbar. A mixture consisting of ~2% of phosphine (B.O.C. Gases, 99.999%) in argon and held at a total pressure of 3 bar was pulsed down the outer of the two concentric, nearly coterminal tubes of the mixing nozzle by means of a Series 9 solenoid valve (Parker-Hannifin) operating at a rate of 3 Hz. Complexes $H_3P\cdots BrCl$ formed at the interface of the two gas flows were polarized with 1.2 μs microwave pulses and the ensuing free induction decay at rotational transition frequencies was detected and processed as described elsewhere.[15] Individual nuclear quadrupole components had a full width at half maximum of ~20 kHz, which allowed frequencies to be measured to within 2 kHz.

d_3-Phosphine was prepared[18] by the action of a dilute solution of DCl in D_2O on calcium phosphide (Sigma-Aldrich) in vacuum. The solution of DCl in D_2O was obtained by diluting a concentrated DCl/D_2O solution (Aldrich, 37% by weight DCl) with D_2O (Apollo Scientific Ltd) in the volume ratio of 1:3.

III. RESULTS

A. Observed spectra and determination of spectroscopic constants

Each of the isotopomers $H_3P\cdots{}^{79}Br^{35}Cl$, $H_3P\cdots{}^{81}Br^{35}Cl$, $H_3P\cdots{}^{79}Br^{37}Cl$, $H_3P\cdots{}^{81}Br^{37}Cl$, $D_3P\cdots{}^{79}Br^{35}Cl$, and $D_3P\cdots{}^{81}Br^{35}Cl$ of the phosphine/bromine monochloride complex exhibited a rotational spectrum characteristic of the ground state of a symmetric-top molecule. Moreover, each $J+1\leftarrow J$ transition consisted of an extensive hyperfine structure that confirmed the presence of the nuclei Br and Cl on the unique axis of the top. Of the several $J+1\leftarrow J$, $K\leftarrow K$ transitions possible for such a complex only those involving $K=0$ and $K=1$ had observable intensity. This observation is readily understood in terms of depopulation of states having $K=2$ and greater during the supersonic expansion through collisional transfer, as moderated by propensity rules of the type discussed elsewhere.[19] Measured frequencies of individual hyperfine components are recorded in Tables I and II.

For each isotopomer, the determinable spectroscopic constants were obtained from observed frequencies by a standard iterative, nonlinear least-squares analysis using the computer program SPFIT, written and supplied by Pickett.[20] A fit having a standard deviation σ of the same magnitude as the estimated accuracy of frequency measurement was possible by constructing a Hamiltonian H having the form

$$H=H_R-1/6\mathsf{Q}_{Br}:\nabla\mathsf{E}_{Br}-1/6\mathsf{Q}_{Cl}:\nabla\mathsf{E}_{Cl}+\mathbf{I}_{Br}\cdot\mathbf{M}_{Br}\cdot\mathbf{J}. \quad (2)$$

In Eq. (2), H_R is the familiar energy operator for a semirigid, prolate symmetric-top molecule, the terms $-1/6\mathsf{Q}_X:\nabla\mathsf{E}_X$ describe the coupling of the halogen nuclear spin angular momentum $\mathbf{I}_X$ to the framework rotational angular momentum $\mathbf{J}$ through the interaction of the nuclear electric quadrupole moment Q_X of X with the electric field gradient $\nabla\mathsf{E}_X$ at X, and the final term accounts for the magnetic coupling of $\mathbf{I}_{Br}$ to $\mathbf{J}$. The corresponding spin-rotation coupling term for Cl was found to be unnecessary for a satisfactory fit. For a symmetric-top molecule, only the components $\chi_{aa}(X)=(eQ/h)\partial^2V_X/\partial a^2$ of the halogen nuclear quadrupole coupling tensors and $M_{aa}(Br)$ and $M_{bb}(Br)=M_{cc}(Br)$ of the spin-rotation coupling tensor $\mathbf{M}_{Br}$ are in principle determinable from the observed transitions and, of these, $M_{aa}(Br)$ was not well determined. In the case of $H_3P\cdots{}^{79}Br^{37}Cl$ this quantity was preset to its value in $H_3P\cdots{}^{79}Br^{35}Cl$. The coupled symmetric-rotor basis $\mathbf{I}_{Br}+\mathbf{J}=\mathbf{F}_1$, $\mathbf{F}_1+\mathbf{I}_{Cl}=\mathbf{F}$ was chosen to construct the matrix of H in view of the relative magnitude $|\chi_{aa}(Br)|>|\chi_{aa}(Cl)|$ of the halogen nuclear quadrupole coupling constants.

Values of the determined spectroscopic constants for each of the six isotopomers of $H_3P\cdots BrCl$ from the final cycle of the least-squares fit are recorded in Table III. The corresponding frequency residuals $\Delta\nu=\nu_{obs}-\nu_{calc}$ are included in Tables I and II. It should be noted that σ is in each case less than, or of comparable magnitude to, the estimated accuracy (2 kHz) of frequency measurement.

B. Inter- and intramolecular electron transfer on formation of $H_3P\cdots BrCl$

The Townes–Dailey model[8,9] for interpreting nuclear quadrupole coupling constants offers a simple and direct means of estimating the changes in the electronic populations associated with the X and Y nuclei in the dihalogen molecule XY when a complex $B\cdots XY$ is formed. In view of the definitions $\chi_{zz}^{e}(X)=(eQ/h)\partial^2V_X/\partial z^2$ and $\chi_{zz}^{e}(Y)=(eQ/h)\partial^2V_Y/\partial z^2$ of the equilibrium nuclear quadrupole coupling constants along the XY internuclear axis z, it is clear that $\chi_{zz}^{e}(X)$ and $\chi_{zz}^{e}(Y)$ of the complex $B\cdots XY$ provide a direct measurement of the electric field gradients (efgs) along z. The values of $\chi_{zz}^{e}(X)$ and $\chi_{zz}^{e}(Y)$ will in general be different from the corresponding zero-point values $\chi_0(X)$

TABLE I. Observed and calculated rotational transition frequencies[a] of $H_3P\cdots{}^{79}Br^{35}Cl$, $H_3P\cdots{}^{81}Br^{35}Cl$, $D_3P\cdots{}^{79}Br^{35}Cl$, and $D_3P\cdots{}^{81}Br^{35}Cl$.

									$H_3P\cdots{}^{79}Br^{35}Cl$		$H_3P\cdots{}^{81}Br^{35}Cl$		$D_3P\cdots{}^{79}Br^{35}Cl$		$D_3P\cdots{}^{81}Br^{35}Cl$	
J'	←	J''	K	$2F_1'$	$2F'$	←	$2F_1''$	$2F''$	ν_{obs} (MHz)	$\Delta\nu$ (kHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)
4	←	3	0	11	13	←	9	11	8800.5822	0.5	8800.7152	0.12	8179.5297	2.6	8178.9894	1.9
			0	11	11	←	9	9	8799.8605	−1.6	⋯	⋯	8178.8139	0.3	8178.2817	0.9
			0	11	9	←	9	7	8798.9777	1.3	8799.1221	0.8	8177.9313	−2.2	8177.4020	−2.0
			0	11	7	←	9	5	8799.8377	1.3	8800.0017	−1.0	⋯	⋯	8178.2799	4.5
			0	9	11	←	7	9	8801.0612	1.2	8801.2598	0.2	8179.9815	−0.9	8179.5076	−6.5
			0	9	9	←	7	7	8798.2185	0.6	8798.4607	2.0	8177.1609	0.5	8176.7322	.0
			0	9	7	←	7	5	8797.6282	0.7	8797.7874	0.4	8176.5774	2.0	8176.0667	−0.6
			0	9	5	←	7	3	8800.6183	−4.6	8800.7962	1.1	⋯	⋯	⋯	⋯
			0	7	9	←	5	7	8825.6400	0.7	8822.0392	0.1	8204.4410	−1.6	8200.2078	−0.6
			0	7	7	←	5	5	8821.1429	−0.6	8817.6205	1.1	8199.9640	−0.2	8195.8111	1.8
			0	7	5	←	5	3	8821.2833	−0.2	8817.7532	0.1	8200.1131	0.5	⋯	⋯
			0	7	3	←	5	1	8825.6798	3.7	8822.0681	−0.9	⋯	⋯	⋯	⋯
			0	5	7	←	3	5	8827.1693	−0.7	8823.2634	0.5	8206.0593	−1.2	⋯	⋯
			0	5	5	←	3	3	8823.2340	−2.5	8819.3610	−0.8	⋯	⋯	⋯	⋯
			0	5	3	←	3	1	8819.5380	−0.8	8815.6364	−1.1	⋯	⋯	⋯	⋯
			1	11	13	←	9	11	8794.9893	−1.0	8796.1014	1.5	8173.8937	1.1	8174.3268	
			1	11	11	←	9	9	8792.4780	−1.3	8793.5812	0.3	8171.4035	−0.2	8171.8301	1.8
			1	11	9	←	9	7	8792.3233	0.0	8793.4345	0.9	8171.2490	0.3	8171.6827	1.3
			1	11	7	←	9	5	8794.8901	−0.3	8796.0215	−2.4	8173.7900	−1.2	8174.2444	−1.7
			1	9	11	←	7	9	8816.2848	−0.1	⋯	⋯	8195.0942	2.2	8192.2770	−0.7
			1	9	9	←	7	7	8812.3325	0.2	8810.2545	3.7	8191.1512	−0.7	8188.4238	2.2
			1	9	7	←	7	5	8812.4605	−0.4	8810.2889	−1.7	8191.2868	−0.6	8188.4645	−4.0
			1	9	5	←	7	3	8816.6658	−1.4	8814.4732	−1.2	⋯	⋯	⋯	⋯
			1	7	9	←	5	7	8828.0068	−1.2	8823.8543	−2.0	8206.8257	0.8	8202.0187	−0.7
			1	7	7	←	5	5	8823.2883	−3.1	8819.2036	1.2	8202.1395	1.6	8197.3952	0.6
			1	7	5	←	5	3	8823.8548	6.0	8819.7504	−0.2	⋯	⋯	⋯	⋯
			1	7	3	←	5	1	8828.6998	−0.2	8824.5740	−0.9	⋯	⋯	⋯	⋯
			1	5	7	←	3	5	8805.0352	0.7	8804.9514	−2.2	8183.7501	−3.1	8183.0503	0.7
			1	5	5	←	3	3	8800.6624	0.4	⋯	⋯	⋯	⋯	⋯	⋯
5	←	4	0	13	15	←	11	13	11 003.7297	−0.6	11 003.3582	−0.4	10 227.4075	−0.5	10 226.2030	2.2
			0	13	13	←	11	11	11 003.3137	−2.7	11 002.9512	1.6	10 226.9978	0.3	10 225.7930	−1.9
			0	13	11	←	11	9	11 002.6165	0.2	11 002.2455	−1.7	10 226.3024	0.7	10 225.0920	−5.0
			0	13	9	←	11	7	11 003.1222	0.3	11 002.7675	0.6	10 226.8010	−1.6	10 225.6118	0.0
			0	11	13	←	9	11	11 004.0026	0.7	11 003.6677	−0.4	10 227.6682	1.6	10 226.5045	4.5
			0	11	11	←	9	9	11 002.4955	0.7	11 002.1992	1.6	⋯	⋯	10 225.0408	1.9
			0	11	9	←	9	7	11 001.8208	0.1	11 001.4677	0.5	10 225.4995	−1.8	10 224.3157	0.6
			0	11	7	←	9	5	⋯	⋯	11 002.9805	−1.6	⋯	⋯	⋯	⋯
			0	9	11	←	7	9	11 018.5786	0.4	11 015.9795	−0.4	10 242.1753	0.9	10 238.7638	1.1
			0	9	9	←	7	7	11 016.3570	0.1	11 013.7995	−0.4	10 239.9648	0.8	10 236.5922	−1.2
			0	9	7	←	7	5	11 015.8537	3.3	11 013.3160	0.9	10 239.4628	0.0	10 236.1112	−2.0
			0	9	5	←	7	3	11 017.8637	0.0	⋯	⋯	⋯	⋯	⋯	⋯
			0	7	9	←	5	7	11 019.1943	0.1	11 016.4903	−1.9	10 242.8250	−0.5	10 239.2979	0.1
			0	7	7	←	5	5	11 017.5390	0.7	11 014.8390	−1.6	10 241.1790	2.1	10 237.6535	−0.8
			0	7	5	←	5	3	11 015.3853	−1.5	11 012.6938	−0.4	10 239.0415	−1.7	10 235.5261	1.1
			0	7	3	←	5	1	11 016.9153	−0.3	11 014.1940	−0.1	⋯	⋯	⋯	⋯
			1	13	15	←	11	13	11 000.5284	0.6	11 000.7067	−0.8	10 224.1425	−0.4	10 223.4860	1.2
			1	13	13	←	11	11	10 999.1616	−0.4	10 999.3405	−0.3	10 222.7878	−0.8	10 222.1258	−3.5
			1	13	11	←	11	9	10 998.7924	−0.4	10 998.9705	−1.2	10 222.4207	−0.5	10 221.7619	−0.1
			1	13	9	←	11	7	11 000.2148	−1.2	11 000.4092	0.0	10 223.8303	−1.0	10 223.1872	0.5
			1	11	13	←	9	11	11 011.2900	0.3	11 009.8249	1.1	10 234.8582	1.2	10 232.5677	0.6
			1	11	11	←	9	9	11 009.0610	−0.6	11 007.6494	1.2	10 232.6407	1.2	10 230.4007	−1.1
			1	11	9	←	9	7	11 008.7186	2.3	11 007.2427	0.3	10 232.3002	1.2	⋯	⋯
			1	11	7	←	9	5	11 011.0185	−1.0	11 009.5326	−0.4	10 234.5902	0.2	⋯	⋯
			1	9	11	←	7	9	11 021.0750	−0.2	11 018.0017	1.2	10 244.6280	−2.5	10 240.7371	1.9
			1	9	9	←	7	7	11 018.3640	−1.4	11 015.3372	0.8	10 241.9368	0.5	10 238.0871	0.8
			1	9	7	←	7	5	11 018.1657	−0.4	11 015.1512	0.0	10 241.7363	−3.1	10 237.9038	0.7
			1	9	5	←	7	3	11 020.7925	−0.7	11 017.7412	−0.1	⋯	⋯	⋯	⋯
			1	7	9	←	5	7	11 009.7599	0.8	11 008.6836	2.5	10 233.2843	4.2	10 231.3905	−1.6
			1	7	7	←	5	5	11 007.4932	−0.8	11 006.4025	−0.5	10 231.0350	−0.1	⋯	⋯
			1	7	5	←	5	3	11 005.9758	−0.4	11 004.9004	0.3	10 229.5247	−0.3	⋯	⋯
			1	7	3	←	5	1	11 008.1429	1.8	11 007.0597	−0.3	⋯	⋯	⋯	⋯

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

TABLE II. Observed and calculated rotational transition frequencies[a] of $H_3P\cdots{}^{79}Br^{37}Cl$ and $H_3P\cdots{}^{81}Br^{37}Cl$.

									$H_3P\cdots{}^{79}Br^{37}Cl$		$H_3P\cdots{}^{81}Br^{37}Cl$	
J'	←	J''	K	$2F_1'$	$2F'$	←	$2F_1''$	$2F''$	ν_{obs} (MHz)	$\Delta\nu$ (kHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)
4	←	3	0	11	13	←	9	11	8596.9059	−1.6	8597.3829	0.0
			0	11	11	←	9	9	8596.3292	−2.4	8596.8075	−3.6
			0	11	9	←	9	7	8595.6336	−1.2	8596.1149	−1.6
			0	11	7	←	9	5	8596.2970	0.4	⋯	⋯
			0	9	11	←	7	9	8597.2336	0.6	8597.7791	−0.5
			0	9	9	←	7	7	⋯	⋯	8595.5289	0.7
			0	9	7	←	7	5	8594.5595	−0.8	⋯	⋯
			0	9	5	←	7	3	⋯	⋯	⋯	⋯
			0	7	9	←	5	7	8621.6937	2.9	8618.4716	0.4
			0	7	7	←	5	5	⋯	⋯	⋯	⋯
			0	7	5	←	5	3	⋯	⋯	⋯	⋯
			0	7	3	←	5	1	⋯	⋯	⋯	⋯
			0	5	7	←	3	5	⋯	⋯	⋯	⋯
			0	5	5	←	3	3	⋯	⋯	⋯	⋯
			0	5	3	←	3	1	⋯	⋯	⋯	⋯
			1	11	13	←	9	11	8591.1961	2.9	8592.6459	2.4
			1	11	11	←	9	9	⋯	⋯	8590.6544	−0.2
			1	11	9	←	9	7	⋯	⋯	8590.5391	1.9
			1	11	7	←	9	5	⋯	⋯	⋯	⋯
			1	9	5	←	7	9	⋯	⋯	8610.5524	0.5
			1	9	9	←	7	7	⋯	⋯	⋯	⋯
			1	9	7	←	7	5	⋯	⋯	⋯	⋯
			1	9	5	←	7	3	⋯	⋯	⋯	⋯
			1	7	9	←	5	7	⋯	⋯	⋯	⋯
			1	7	7	←	5	5	⋯	⋯	⋯	⋯
			1	7	5	←	5	3	⋯	⋯	⋯	⋯
			1	7	3	←	5	1	⋯	⋯	⋯	⋯
			1	5	7	←	3	5	⋯	⋯	⋯	⋯
			1	5	5	←	3	3	⋯	⋯	⋯	⋯
5	←	4	0	13	15	←	11	13	10 749.2146	0.2	10 749.2771	2.7
			0	13	13	←	11	11	10 748.8822	−1.1	10 748.9452	−0.5
			0	13	11	←	11	9	10 748.3364	1.7	10 748.3979	2.1
			0	13	9	←	11	7	10 748.7222	−0.9	10 748.7929	0.1
			0	11	13	←	9	11	10 749.3977	−1.8	10 749.4997	0.1
			0	11	11	←	9	9	10 748.1888	−0.7	10 748.3056	2.3
			0	11	9	←	9	7	10 747.6977	1.6	10 747.7833	−1.0
			0	11	7	←	9	5	⋯	⋯	⋯	⋯
			0	9	11	←	7	9	10 763.9049	−0.0	10 761.7662	−1.1
			0	9	9	←	7	7	10 762.1352	−0.2	10 760.0164	−0.3
			0	9	7	←	7	5	10 761.7113	−1.9	⋯	⋯
			0	9	5	←	7	3	10 763.3409	0.4	⋯	⋯
			0	7	9	←	5	7	10 764.4806	0.2	10 762.2072	−0.2
			0	7	7	←	5	5	10 763.1770	−1.1	10 760.9095	−0.6
			0	7	5	←	5	3	10 761.4784	6.2	⋯	⋯
			0	7	3	←	5	1	⋯	⋯	⋯	⋯
			1	13	15	←	11	13	10 745.9467	0.7	10 746.5570	1.5
			1	13	13	←	11	11	10 744.8665	0.2	10 745.4739	−0.7
			1	13	11	←	11	9	10 744.5794	2.5	10 745.1833	−2.1
			1	13	9	←	11	7	10 745.6935	1.7	10 746.3056	−4.3
			1	11	13	←	9	11	10 756.6265	−0.7	⋯	⋯
			1	11	11	←	9	9	10 754.8422	0.2	10 753.8425	2.9
			1	11	9	←	9	7	10 754.6122	2.4	10 753.5785	0.5
			1	11	7	←	9	5	10 756.4278	−2.6	10 755.3863	−2.4
			1	9	11	←	7	3	10 766.4029	1.9	10 763.7882	1.2
			1	9	9	←	7	7	10 764.2370	−2.3	10 761.6467	−0.1
			1	9	7	←	7	5	10 764.0675	−0.6	⋯	⋯
			1	9	5	←	7	3	10 766.1640	−3.4	⋯	⋯
			1	7	9	←	5	7	10 755.0179	1.5	10 754.3739	0.6
			1	7	7	←	5	5	10 753.2325	−1.8	10 752.5810	−0.9
			1	7	5	←	5	3	10 752.0270	−2.0	⋯	⋯
			1	7	3	←	5	1	⋯	⋯	⋯	⋯

[a] $\Delta\nu=\nu_{obs}-\nu_{calc}$.

TABLE III. Determined ground-state spectroscopic constant of six isotopomers of the complex $H_3P\cdots BrCl$

Property	Isotopomer					
	$H_3P\cdots{}^{79}Br^{35}Cl$	$H_3P\cdots{}^{81}Br^{35}Cl$	$H_3P\cdots{}^{79}Br^{37}Cl$	$H_3P\cdots{}^{81}Br^{37}Cl$	$D_3P\cdots{}^{79}Br^{35}Cl$	$D_3P\cdots{}^{81}Br^{35}Cl$
B_0 (MHz)	1100.7894(2)	1100.6849(2)	1075.3454(3)	1075.2837(3)	1023.1517(2)	1022.9641(2)
D_J (kHz)	0.584(3)	0.584(3)	0.554(6)	0.544(6)	0.513(4)	0.511(4)
D_{JK} (kHz)	11.51(6)	11.48(6)	11.11(7)	11.03(8)	18.51(7)	18.33(7)
χ_{aa} (Br)(MHz)	881.55(3)	736.46(3)	881.57(6)	736.51(6)	881.13(4)	736.18(4)
χ_{aa} (Cl)(MHz)	−86.988(14)	−87.002(15)	−68.59(3)	−68.59(3)	−86.37(2)	−86.39(2)
M_{aa} (Br)(kHz)	28(8)	5(8)	28[a]	24(15)	17(9)	18(10)
M_{bb} (Br)(kHz)	3.5(4)	3.1(3)	3.2(5)	3.4(6)	3.2(5)	3.3(5)
σ (kHz)[b]	1.5	1.4	1.7	1.7	1.5	2.1
N[c]	60	57	37	32	46	42

[a] Assumed unchanged from $H_3P\cdots{}^{79}Br^{35}Cl$.

[b] Standard deviation of the fit.

[c] Number of transitions included in the fit.

and $\chi_0(Y)$, respectively, of the free molecule XY because the electric charge distribution of XY is perturbed by B and this changes the efgs.

If δ_X and δ_Y are the net increases in the number of valence shell p_z electrons of X and Y, respectively, the Townes–Dailey model leads to the following relations:

$$\chi_{zz}^{e}(X)=\chi_0(X)-\delta_X\chi_A(X), \quad (3)$$

$$\chi_{zz}^{e}(Y)=\chi_0(Y)-\delta_Y\chi_A(Y), \quad (4)$$

where $\chi_A(X)$ and $\chi_A(Y)$ are the nuclear quadrupole coupling constants of the free atoms X and Y, respectively. The equilibrium quantities $\chi_{zz}^{e}(X)$ and $\chi_{zz}^{e}(Y)$ are related to the zero-point observables $\chi_{aa}(X)$ and $\chi_{aa}(Y)$ in reasonable approximation by

$$\chi_{aa}(X)=\chi_{zz}^{e}(X)\langle P_2(\cos\beta)\rangle \quad (5)$$

and

$$\chi_{aa}(Y)=\chi_{zz}^{e}(Y)\langle P_2(\cos\beta)\rangle, \quad (6)$$

where β is the angle between the XY internuclear axis z and the a-axis of the complex and the average of $P_2(\cos\beta)$ is taken over the zero-point motion of XY. The approximation made in writing Eqs. (5) and (6) as exact equalities is that the zero-point coupling constants $\chi_{zz}(X)$ and $\chi_{zz}(Y)$ are unaffected by the oscillation of the B subunit. Equations (3) to (6) can then be combined to give the following expressions for δ_X and δ_Y:

$$\delta_X=\{\chi_0(X)/\chi_A(X)\}-\{\chi_{aa}(X)/\chi_A(X)\}\langle P_2(\cos\beta)\rangle^{-1} \quad (7)$$

and

$$\delta_Y=\{\chi_0(Y)/\chi_A(Y)\}-\{\chi_{aa}(Y)/\chi_A(Y)\}\langle P_2(\cos\beta)\rangle^{-1}. \quad (8)$$

In the case of $H_3P\cdots BrCl$, δ_Y is the increase in the population of the $3p_z$ orbital of Cl as a result of electrons pushed from Br to Cl by H_3P when the complex is formed. To recognize that in the case of $H_3P\cdots BrCl$ this quantity therefore originates in a polarization of BrCl, and is an increase in electron population at Cl, it is written as $\delta_Y=\delta_p^{Cl}$. If a fraction δ_i of an electron undergoes intermolecular transfer from P of PH_3 to the $4p_z$ orbital of Br, we may make the identification $\delta_X=\delta_{Br}=\delta_i-\delta_p^{Cl}$, since the net increase of $4p_z$ electron at Br results from a gain δ_i and a loss δ_p^{Cl}. To obtain δ_i and δ_p^{Cl} from Eqs. (7) and (8) requires a value for $\langle P_2(\cos\beta)\rangle^{-1}$ and this must be estimated.

It turns out that $\beta_{av}=\cos^{-1}\langle\cos^2\beta\rangle^{1/2}$ for $B\cdots BrCl$ complexes is generally small, no doubt because of the relatively large reduced mass for the oscillation. Accordingly, $\langle P_2(\cos\beta)\rangle$ is close to unity. An upper limit to β_{av} for $B\cdots BrCl$ complexes may be estimated as follows. The most weakly bound member of the $B\cdots BrCl$ series so far investigated by rotational spectroscopy is $OC\cdots BrCl$, at least when the intermolecular stretching force constant k_σ (see Sec. III E) is used as a measure of binding strength.[21] If we assume that $\delta_i\approx 0.0$ for the $OC\cdots{}^{79}Br^{35}Cl$ isotopomer of this complex, Eqs. (7) and (8) may be solved to give $\delta_p^{Cl}=0.0250$ and $\beta_{av}=6.79°$, when the known values[22,23] of $\chi_A(Br)$, $\chi_A(Cl)$, $\chi_0(Br)$, and $\chi_0(Cl)$ given in Table IV are employed. Given that $k_\sigma=11.5\ \mathrm{N\,m^{-1}}$ for $H_3P\cdots BrCl$ is $\sim$ twice as large as $k_\sigma=6.3\ \mathrm{N\,m^{-1}}$ for $OC\cdots BrCl$, we expect β_{av} for $H_3P\cdots BrCl$ to be smaller than for the CO analog on the grounds that as the complex becomes more strongly bound, the angular oscillation of the BrCl subunit will be attenuated. We shall assume $\beta_{av}=6.0(5)°$ for $H_3P\cdots BrCl$ and hence $\langle P_2(\cos\beta)\rangle=0.9836(28)$, with the expectation that the actual values will lie somewhere in the ranges assumed.

The values of δ_i and δ_p^{Cl} obtained from Eqs. (7) and (8) under the assumption of $\beta_{av}=6.0(5)°$ are given in Table V for each of the six isotopomers investigated. The range of each of the quantities is that arising from the assumed error in β_{av} and is only 5% of the magnitude even in the case of δ_i, which is the least well determined of the two δ parameters. We note that the intermolecular electron transfer in $H_3P\cdots BrCl$ is substantial and corresponds to about 0.1 of an electron from P to Br. We shall discuss how δ_i varies along the series $B\cdots BrCl$, where B=CO, C_2H_2, H_2O, C_2H_4, H_2S, NH_3, and PH_3, in Sec. IV. In particular, we shall consider a comparison of δ_i between the two series $B\cdots BrCl$ and $B\cdots ICl$.

TABLE IV. Properties of PH_3 and BrCl used in the determination of δ_i, δ_p^{Cl}, r_{cm}, $r(P\cdots Br)$ and k_σ of the $H_3P\cdots BrCl$ complex.

Molecule	B_0 (MHz)	C_0 (MHz)	χ_0 (Br) or χ_A (Br)(MHz)	χ_0 (Cl) or χ_A (Cl)(MHz)	Geometry[a]	
					r (Å)	γ (deg)
PH_3[b]	133 480.1167(17)	117 489.4374(77)	⋯	⋯	1.4200	93.345
PD_3[c]	69 471.145(23)	58 973.960(556)	⋯	⋯	1.4176	93.360
$^{79}Br^{35}Cl$[d]	4 559.3827(1) (4383.7)	4 559.3827(1) (4383.7)	875.309(1)	−102.450(2)	2.13877	⋯
$^{81}Br^{35}Cl$[d]	4 524.8598(1) (4350.5)	4 524.8598(1) (4350.5)	731.223(1)	−102.451(2)	2.13876	⋯
$^{79}Br^{37}Cl$[d]	4 388.9109(1) (4219.6)	4 388.9109(1) (4219.6)	875.304(1)	−80.740(2)	2.13871	⋯
$^{81}Br^{37}Cl$[d]	4 354.3855(1) (4186.4)	4 354.3855(1) (4186.4)	731.219(1)	−80.740(2)	2.13870	⋯
Atomic ^{79}Br[e]	⋯	⋯	769.76	⋯	⋯	⋯
Atomic ^{81}Br[e]	⋯	⋯	643.03	⋯	⋯	⋯
Atomic ^{35}Cl[e]	⋯	⋯	⋯	−109.74	⋯	⋯
Atomic ^{37}Cl[e]	⋯	⋯	⋯	−86.51	⋯	⋯

[a] r_0-geometries determined by fitting principal moments of inertia. Errors arising from rotational constants are not significant relative to number of digits quoted.

[b] Reference 27.

[c] Reference 28.

[d] Reference 23. Values in parentheses are rotational constants appropriate to BrCl at the Br–Cl bond length as it exists in the complex (2.181 Å—see text).

[e] Reference 22.

C. Lengthening of the BrCl bond on formation of $H_3P\cdots BrCl$

Given that there is significant inter- and intramolecular electron transfer when $H_3P\cdots BrCl$ is formed from its components, as indicated by the values of δ_i and δ_p^{Cl} determined in Sec. III B, it is likely that the BrCl bond will lengthen and weaken for the same reason. In fact, the r_s-version of the BrCl internuclear distance can be established in the complex $H_3P\cdots BrCl$ and compared with the free molecule value.

The a-coordinates of the Br and Cl atoms are given by

$$a_i^2=\Delta I_b/\mu_s, \tag{9}$$

where $\mu_s=\Delta mM/(M+\Delta m)$ is the reduced mass for the substitution and ΔI_b is the change in the principal moment of inertia I_b that accompanies isotopic substitution of an atom i on the symmetry axis of a symmetric-top molecule. When zero-point moments of inertia are used in Eq. (9), the quantity a_i is by definition an r_s-coordinate.[24] If $H_3P\cdots{}^{79}Br^{35}Cl$ is chosen as the parent molecule, substitutions of ^{81}Br and ^{37}Cl lead to the coordinates $|a_{Br}|=0.148(4)$ Å and $|a_{Cl}|=2.3480(1)$ Å of Br and Cl referred to the principal axis system of the parent. If a_{Br} and a_{Cl} are assumed to have the same sign, the distance between these atoms in the zero-point state of the complex is 2.200 Å. To allow for the angular oscillation of the BrCl subunit in the complex, we recognize that

$$r_s(Br-Cl)\approx\{|a_{Cl}|-|a_{Br}|\}/\cos\beta_{av}. \tag{10}$$

Use of $\beta_{av}=6.0(5)°$ gives $r_s(Br–Cl)=2.212(6)$ Å, which is longer by $\delta r=0.075$ Å than the corresponding quantity 2.137 38 Å in free BrCl. The choice of opposite signs for a_{Br} and a_{Cl} leads to the physically unreasonable lengthening of 0.372 Å.

TABLE V. Some properties of the complex $H_3P\cdots BrCl$ determined by rotational spectroscopy.

Isotopomer	Property				
	δ_i[a]	δ_p^{Cl}[b]	r_{cm} (Å)[c]	$r(P\cdots Br)$(Å)[d]	k_σ (Nm^{-1})[e]
$H_3P\cdots{}^{79}Br^{35}Cl$	0.101(5)	0.128(2)	3.6071(5)	2.8692(5)	11.56(7)
$H_3P\cdots{}^{81}Br^{35}Cl$	0.100(5)	0.128(2)	3.5955(5)	2.8692(5)	11.62(7)
$H_3P\cdots{}^{79}Br^{37}Cl$	0.100(5)	0.127(2)	3.6336(5)	2.8697(5)	11.37(13)
$H_3P\cdots{}^{81}Br^{37}Cl$	0.100(5)	0.127(2)	3.6218(5)	2.8697(5)	11.65(13)
$D_3P\cdots{}^{79}Br^{35}Cl$	0.106(5)	0.131(2)	3.6484(5)	2.8537(5)	11.48(9)
$D_3P\cdots{}^{81}Br^{35}Cl$	0.106(5)	0.133(2)	3.6374(5)	2.8541(5)	11.53(9)

[a] Fraction of an electron transferred from PH_3 to Br on formation of $H_3P\cdots BrCl$.

[b] Fraction of an electron transferred from Br to Cl on formation of $H_3P\cdots BrCl$. See text for discussion of this interpretation of the polarization of BrCl.

[c] Determined by using Eq. (11).

[d] Determined from r_{cm} with the aid of Eq. (12). See text and Table IV for discussion of I_b^{BrCl}, $I_b^{PH_3}$, and $I_c^{PH_3}$ values employed.

[e] Determined from D_J by using Eq. (13).

The value of $\delta r=0.075$ Å is likely to be an upper limit to this quantity because small r_s-coordinates, such as a_{Br} determined via Eq. (9), are known to be underestimates. This arises because of the well-known shrinkage of bonds involving an atom near to the center of mass when that atom is substituted by an isotope of larger mass.[25] Thus, Cox and Riveros[26] showed that the imaginary value of a_N in $H^{14}NO_3$ obtained from ^{15}N substitution could be made sensible by assuming that the three N–O bonds shrink by 8×10^{-5} Å on ^{15}N substitution. It is of interest to recalculate a_{Br} in $H_3P\cdots{}^{79}Br^{35}Cl$ by assuming that the $P\cdots Br$ and Br–Cl bonds shrink by 5×10^{-5} and 1×10^{-5} Å, respectively when ^{79}Br is substituted by ^{81}Br. The shrinkage assumed for Br–Cl is the difference in r_0(Br–Cl) between free $^{79}Br^{35}Cl$ and $^{81}Br^{35}Cl$ (see Table IV), while that for $P\cdots Br$ is a reasonable

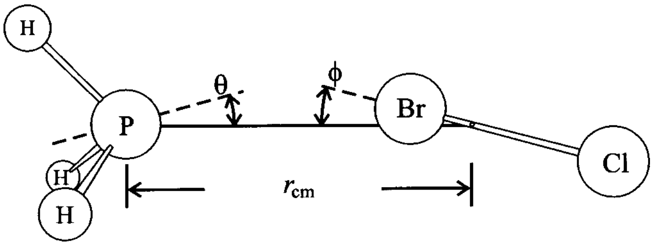

FIG. 1. Definition of the distance r_{cm} and the angles θ and ϕ used in the discussion of the geometry of $H_3P\cdots BrCl$.

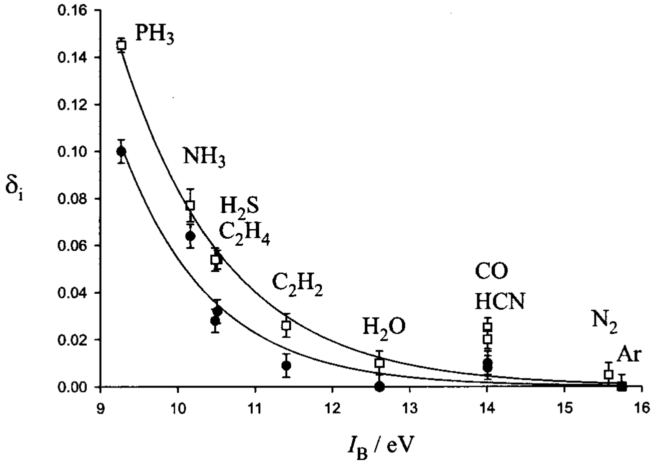

FIG. 2. Variation of the fraction of an electron δ_i transferred from the donor atom of B to Br on formation of complexes $B\cdots BrCl$ with the ionization energy I_B of the Lewis base B (solid circles). The open squares indicate the values of δ_i for the series $B\cdots ICl$. The lines drawn through the points are $\delta_i = A\exp(-bI_B)$, with $A = 327.5$ and $b = 0.870\,(\mathrm{eV})^{-1}$ for the $B\cdots BrCl$ series and $A = 128.5$ and $b = 0.734\,(\mathrm{eV})^{-1}$ for the $B\cdots ICl$ series.

value for a weak bond. The procedure to allow for shrinkage in $H_3P\cdots{}^{79}Br^{35}Cl$ that accompanies ^{81}Br substitution is then as follows.

First, I_b for $H_3P\cdots{}^{79}Br^{35}Cl$ was fitted to give $r(P\cdots Br)$ under the assumption of unchanged monomer geometries (see Table IV).[23,27,28] This value of $r(P\cdots Br)$ was then used to estimate I_b for $H_3P\cdots{}^{81}Br^{35}Cl$. The $P\cdots Br$ and Br–Cl distances were next shrunk by 5×10^{-5} and 1×10^{-5} Å, respectively and I_b' of $H_3P\cdots{}^{81}Br^{35}Cl$ was recalculated. Then the correction $\Delta I_b^{\mathrm{corr}} = I_b' - I_b$ was added to I_b^{obs} for $H_3P\cdots{}^{81}Br^{35}Cl$ to correct for bond shrinkage. The corrected I_b^{obs} used in Eq. (9) led to a corrected coordinate $|a_{\mathrm{Br}}| = 0.167(4)$ Å. Accordingly, Eq. (10) gives $r_s(\mathrm{Br–Cl}) = 2.181(6)$ Å after correction for shrinkage effects and corresponds to a lengthening $\delta r = 0.044(6)$ Å on formation of $H_3P\cdots BrCl$. The same treatment applied earlier[21] to $OC\cdots BrCl$ gives $\delta r = 0.020$ Å. Thus the more weakly bound $OC\cdots BrCl$ ($k_\sigma = 6.3\,\mathrm{N\,m^{-1}}$) has a smaller lengthening δr of the BrCl bond than $H_3P\cdots BrCl$ ($k_\sigma = 11.5\,\mathrm{N\,m^{-1}}$), which seems physically reasonable.

D. The distance $r(P\cdots Br)$ in $H_3P\cdots BrCl$

The ground-state rotational spectra attributed to the isotopomers $H_3P\cdots{}^{79}Br^{35}Cl$, $H_3P\cdots{}^{81}Br^{35}Cl$, $H_3P\cdots{}^{79}Br^{37}Cl$, $H_3P\cdots{}^{81}Br^{37}Cl$, $D_3P\cdots{}^{79}Br^{35}Cl$, and $D_3P\cdots{}^{81}Br^{35}Cl$ are all of the symmetric-top type. There are four possible arrangements of the subunits which lead to a complex of C_{3v} symmetry, namely $H_3P\cdots BrCl$, $PH_3\cdots BrCl$, $H_3P\cdots ClBr$, and $PH_3\cdots ClBr$. The third and fourth of these can be ruled out by the relative magnitudes of the r_s-coordinates a_{Br} and a_{Cl} established in the preceding section. Of the remaining two possibilities, only $H_3P\cdots BrCl$ is consistent with the magnitude of the changes in the rotational constants B_0 on isotopic substitution of H_3 by D_3.

Given the established order of the nuclei $H_3P\cdots BrCl$ and C_{3v} symmetry, the distance $r(P\cdots Br)$ between the atoms directly involved in the weak interaction can be established as follows. We assume the contribution of the intermolecular bending modes to the zero-point motion of the complex can be modeled by allowing the PH_3 and BrCl subunits to execute angular oscillations θ and ϕ, respectively, as defined in Fig. 1. The motion of each subunit is pivoted at its mass center and the appropriate angle is that made by the symmetry axis of the subunit (C_3 for PH_3; C_∞ for BrCl) with the line r_{cm} joining the two mass centers. If the intermolecular stretching motion is ignored, it can be shown[29] that

$$I_b^0 \approx \langle I_{bb}\rangle = \mu r_{cm}^2 + 1/2 I_b^{PH_3}\langle 1+\cos^2\theta\rangle + 1/2 I_c^{PH_3}\langle \sin^2\theta\rangle + 1/2 I_b^{BrCl}\langle 1+\cos^2\phi\rangle, \tag{11}$$

where $\mu = m^{PH_3}m^{BrCl}/(m^{PH_3}+m^{BrCl})$ and the angular brackets indicate the average over the zero-point motion. The quantities $I_b^{PH_3}$, $I_c^{PH_3}$, and I_b^{BrCl} are strictly the principal moments of inertia of the subunits appropriate to their geometries within the complex, although often unchanged monomer geometries are assumed. In the present case, the value of I_b^{BrCl} for BrCl as it exists within the complex is available because $r_s(\mathrm{BrCl})$ has been determined (see Sec. III C). The values of $I_b^{PH_3}$ and $I_c^{PH_3}$ appropriate to the geometry of PH_3 when bound in the complex are not known but fortunately r_{cm} determined via Eq. (11) is insensitive to changes in the P–H distance, R, and the HPH angle, γ, of PH_3. Thus $(\partial r_{cm}/\partial R)_\gamma = -2.85\times10^{-2}$ and $(\partial r_{cm}/\partial\gamma)_R = 1.85\times10^{-4}$ Å deg^{-1}. Accordingly, the moments of inertia of PH_3 were taken as unchanged[27,28] by complex formation (available from Table IV). The error thereby introduced into r_{cm} is likely to be negligible unless large changes in the PH_3 geometry occur.

Values of r_{cm} determined for each isotopomer of $H_3P\cdots BrCl$ by applying Eq. (11) are listed in Table V. The angles $\theta_{av} = \cos^{-1}\langle\cos^2\theta\rangle^{1/2} = 15(10)°$ and $\phi_{av} = \cos^{-1}\langle\cos^2\phi\rangle^{1/2} = 6.0(5)°$ were employed. It can be shown[30] that $\langle\cos^2\beta\rangle = \langle\cos^2\phi\rangle$ and the choice of $\beta_{av} = 6.0(5)°$ was justified in Sec. III C. The value of r_{cm} is insensitive to the choice of the angle θ_{av} because PH_3 is not far from the spherical top limit. An assumed range $\theta_{av} = 15(10)°$, which we confidently expect to include the actual value, leads to a range of only $\pm 8\times10^{-4}$ Å in r_{cm}. Also included in Table V is the distance $r(P\cdots Br)$ for each isotopomer, as determined from r_{cm} by means of

$$r(P\cdots Br) = r_{cm} - r - r', \tag{12}$$

where r and r' are the distances of the P and Br atoms from the PH_3 and BrCl centers of mass, respectively. Values of r and r' appropriate to unperturbed PH_3 isotopomers and BrCl at its geometry in the complex are available from the geometries included in Table IV.

We note from Table V that $r(P\cdots Br)$ is significantly shorter for $D_3P\cdots BrCl$ isotopomers than for $H_3P\cdots BrCl$ isotopomers. A similar effect has been observed in the complexes $H_3P\cdots ICl$[11] and $H_3P\cdots HCl$.[31] A possible source of the effect is the increased electric dipole moment[32] of PD_3 relative to PH_3 and therefore an increased interaction strength in $D_3P\cdots BrCl$ isotopomers, as discussed elsewhere.[11] We also note that both δ_i and δ_p^{Cl} (see Table V) appear larger in the $D_3P\cdots BrCl$ species, indicating an enhanced interaction.

E. Strength of the intermolecular bond in $H_3P\cdots BrCl$

We can gauge the strength of the intermolecular binding in $H_3P\cdots BrCl$ from the magnitude of the intermolecular stretching force constant k_σ, which in the approximation that terms higher than quadratic in the force field of the complex are negligible gives the restoring force for unit infinitesimal displacement along the C_3 axis. k_σ is inversely related to the centrifugal distortion constant D_J in the quadratic approximation by the expression[33]

$$k_\sigma=(16\pi^2B_0^3\mu/D_J)\{1-(B_0/B^{PH_3})-(B_0/B^{BrCl})\}, \qquad (13)$$

where B_0, B^{PH_3}, and B^{BrCl} are rotational constants of the complex, the PH_3 subunit, and the BrCl subunit, respectively, and μ has been defined in Sec. III D. Values of k_σ estimated by means of Eq. (13) for the various isotopomers of $H_3P\cdots BrCl$ investigated are included in Table V. The D_J and B_0 values were taken from Table III while B^{PH_3} appropriate to the free PH_3 molecule, as given in Table IV, was employed. In view of the lengthened BrCl bond within the complex established in Sec. III D, B^{BrCl} for the free molecule was considered inappropriate and the value of this constant calculated for the bond length $r_s=2.181(2)$ Å of BrCl when within the complex was taken instead. In fact, use of the free molecule value of B^{BrCl} would lead to only small changes in the estimated k_σ values compared with the errors that arise from those in D_J and systematic shortcomings of the model. We note from Table V that k_σ is almost isotopically invariant within experimental error. The magnitude of k_σ establishes that, according to this criterion, $H_3P\cdots BrCl$ is not a strongly bound complex and that it is comparable in binding strength with $C_2H_4\cdots BrCl$,[34] and $HCN\cdots BrCl$,[35] for example. On the other hand, the intermolecular electron transfer δ_i in $H_3P\cdots BrCl$ is significantly greater than in $C_2H_4\cdots BrCl$ and $HCN\cdots BrCl$ (see Sec. IV).

IV. DISCUSSION

This investigation of the ground-state rotational spectra of six isotopomers of the phosphine–bromine monochloride complex has established that the molecule has C_{3v} symmetry and that the intermolecular bond is formed between P and Br, with a distance $r(P\cdots Br)=2.869(1)$ Å. The interaction of the two component molecules is not particularly strong [$k_\sigma=11.5(1)$ N m^{-1}] and it has been established that there is a relatively small lengthening of the BrCl bond on formation of the complex. By contrast, interpretations of the Br and Cl nuclear quadrupole coupling constants, based on a simple version of the Townes–Dailey model, reveal that not only is there a significant intramolecular electronic transfer from Br to Cl on complex formation [i.e., $\delta_p^{Cl}=0.128(2)$] but there is also a substantial intermolecular transfer. Indeed, it was shown that a fraction $\delta_i=0.10(1)$ of an electron moves from P to Br.

One might expect that a large extent of electron transfer would imply a stronger intermolecular bond but evidently this is not the case for the pair of isostructural complexes $H_3P\cdots BrCl$ and $H_3N\cdots BrCl$. For example, application of the analysis of the halogen nuclear quadrupole coupling constants described in Sec. III B gives $\delta_i=0.064(5)$ for $H_3N\cdots BrCl$,[36] but this complex is much more strongly bound than $H_3P\cdots BrCl$, the k_σ values being 26.7(3) and 11.7(1) N m^{-1}, respectively. What is it that controls the magnitude of δ_i?

The extent of intermolecular electron transfer δ_i in complexes $B\cdots ICl$ has been shown[10] to correlate with the appropriate ionization energy I_B of the Lewis base B. In this context, the word ''appropriate'' implies that I_B refers to removal of an electron from the orbital (nonbonding σ-type or π-type) directly involved in the intermolecular interaction. In fact, for a series of ten complexes $B\cdots ICl$, the variation of δ_i with I_B is well described by the expression $\delta_i=A\times\exp\{-bI_B\}$, as discussed in Sec. I. It is of interest to examine whether similar behavior is also manifest in the $B\cdots BrCl$ series.

The Br and Cl nuclear quadrupole coupling constants $\chi_{aa}(Br)$ and $\chi_{aa}(Cl)$ are now available for eight complexes $B\cdots BrCl$, namely those having B=CO,[7] HCN,[35] H_2O,[37] C_2H_2,[38] C_2H_4,[34] H_2S,[39] NH_3,[36] or PH_3. Hence, values of δ_i for these complexes can be estimated by using the procedure set out in Sec. III B. The results are shown in Fig. 2, in which δ_i is plotted against I_B, as obtained from Refs. 13 and 40. In each case, we used the angle $\beta_{av}=6.0(5)°$ for reasons set out in detail in Sec. III B. Although $Ar\cdots BrCl$ is not among the complexes so far investigated, we have assumed $\delta_i=0.0$ and therefore taken this complex as the reference point. The error bars on the δ_i values given in Fig. 2 are those generated by the assumed range in β_{av}. The solid line is the curve $\delta_i=A\exp\{-bI_B\}$, where $A=327.5$ and $b=0.870\,(\text{eV})^{-1}$, which has been fitted to the points by the least-squares method.

The corresponding curve for ten complexes $B\cdots ICl$, established earlier,[10] is also displayed in Fig. 2. We note that some points, particularly those for $H_3N\cdots BrCl$ and the CO/HCN pair in both $B\cdots BrCl$ and $B\cdots ICl$, deviate from the curve fitted to Eq. (1). This probably arises from the limitations of the Townes–Dailey model when applied in this context. Nevertheless, we can discern a strong family relationship between the $B\cdots ICl$ and $B\cdots BrCl$ curves, but we recognize that, for a given B, the value of δ_i for $B\cdots BrCl$ is systematically smaller than that of $B\cdots ICl$. There are two obvious reasons for the order $\delta_i(B\cdots ICl)>\delta_i(B\cdots BrCl)$. The first is that the electric dipole moment of ICl (1.24 D)[41] is greater than that of BrCl (0.519 D),[42] so that distortion of the electron-donor orbital of the Lewis base by ICl is likely to be the greater. Alternatively, I in ICl is generally assumed to be a better electron acceptor than Br in BrCl. The corresponding δ_i versus I_B curves for other series of complexes B···XY, for example XY=Cl_2 or Br_2, are clearly of interest in this context.

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